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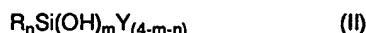
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(54) Microcapsule having a specific wall and method for producing the same

(57) A microcapsule containing core material and a capsule wall, in which the capsule wall of the microcapsule comprises:

organopolysiloxane synthesized by polycondensing one or more compounds represented by the general formula (II):



wherein, m represents an integer from 1 to 4; n represents an integer from 0 to 3; $m+n \leq 4$; R represents an organic group in which a carbon atom is directly connected to a silicone atom, and when n is greater than 1, each of the R groups may be the same or different; and Y represents at least one group selected from the group consisting of an alkoxy group, hydrogen and siloxy group, and when $(4-m-n)$ is greater than 1, each of the groups Y may be the same or different; provided that compound (B) comprises at least one compound of formula (II) wherein $m=2$ or 3 and at least one of R group possesses affinity for at least one of a continuous phase and a dispersed phase; a method for producing the microcapsule; and a use of the microcapsule, for example for cosmetics are provided.

Description

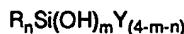
- [0001] The present invention relates to a microcapsule that contains a core material and a method for producing the same. More particularly, the present invention relates to a microcapsule, which has a capsule wall composed of organopolysiloxane obtained by polycondensation of a specific hydroxysilane, having thermal and mechanical stability and light resistance and which is bio-inactive.
- [0002] The microcapsule of the present invention is applied, for example, to pharmaceuticals, liquid crystal, chemical products, recording materials, cosmetic compositions, aromatics, enzymes, agriculture, adhesives, fiber, foods, catalysts, detergents, dyes, paints, preservatives and solvents. Specific examples thereof include microcapsules containing aspirin, vitamins or liquid crystals, pressure sensitive manifold paper, a capsule containing ultraviolet ray absorbers, coloring matters, pigments, aromatics, menthol, insecticides or adhesives and a capsule containing a preservative for rivet, although use of the microcapsule is not limited to the above-mentioned uses.
- [0003] Application of organopolysiloxanes in a wide range of fields is expected since they have excellent properties such as thermal and mechanical stability and light resistance, and bio-inactivity as general basic properties. Also in the field of microcapsules, such as a microcapsule in the narrow sense and a nanocapsule, production of microcapsules has been previously tried using a capsule walls composed of a polysiloxane or an analogous material.
- [0004] For example, US-Patent No. 3257330 discloses a method for producing a colored gel particle comprising organopolysiloxane as a matrix. However, when an alkoxysilane having a hydrophobic organic group, such as methyltriethoxsilane, is used as a starting material of the matrix, is hydrolyzed and then neutralized, the polymer composition forms a deposit in an aqueous solution. As a result, it has been difficult to produce a microcapsule by incorporating a hydrophobic core material with the polymerization of a hydrolyzate of an alkoxysilane in the aqueous solution.
- [0005] On the other hand, US-Patent No. 3551346 teaches a method in which a polysiloxane is synthesized from a trialkoxysilane in the production of a microcapsule. However, the polysiloxane does not have sufficient strength as a capsule wall (as admitted by this US-Patent). Therefore, this US-Patent discloses a method for producing a microcapsule having a capsule wall of a two-layer structure by further making simultaneously a capsule wall by a conventional coacervation method. In addition, it is believed that any more than a certain amount a trialkoxysilane can not be used for producing a capsule wall since the trialkoxysilane is confined in an inner phase by the newly generated polysiloxane capsule wall. Therefore, this method is not admitted as a general method for producing a microcapsule composed only of the polysiloxane capsule wall.
- [0006] Further, JP-B-60-25185, JP-B-3-10309, JP-B-5-70496 and JP-B-7-62109 disclose examples wherein a wall of a microcapsule is produced by cross-linking a polysiloxane having a functional group which can participate in cross-linking and polymerization. However, it is difficult to handle such a specific polysiloxane having a functional group participating in cross-linking and polymerization.
- [0007] As described above, it has been difficult to easily produce a microcapsule having a capsule wall composed of organopolysiloxane according to conventional technologies.
- [0008] It is advantageous also in cost to directly produce a microcapsule by making, from a hydroxysilane precursor having various properties, an organopolysiloxane capsule wall that can utilize such properties. Further, microcapsules suited for an object can be easily designed by combining various hydroxysilane precursors. For example, they can be expected to produce various capsule walls such as a capsule wall having tight compact network, a capsule wall having an appropriate permeation property, or a capsule wall having high strength or being suitably soft. However, it has been difficult to produce a microcapsule while controlling conditions such as polymerization rate and solubility when solely using a hydroxysilane precursor having a low molecular weight.
- [0009] An object of the present invention is to provide a microcapsule that contains a core material, wherein the microcapsule contains a capsule wall composed of organopolysiloxane having excellent properties. Another object of the present invention is to provide a method for producing such a microcapsule easily and with high productivity from generally available silicon compounds.
- [0010] The present inventors have intensively studied a method for producing a microcapsule having a capsule wall composed of organopolysiloxane directly from a hydroxysilane precursor in order to solve the above-described problems. As a result, the inventors have found that the above-described object can be attained if: one or more compounds (A) selected from the group of compounds represented by the following general formula (I)



Formula (I)

wherein n represents an integer from 0 to 3; R represents an organic group in which a carbon atom is directly connected to a silicone atom, and when n is greater than 1, each of the R groups may be the same or different; and X represents at least one group selected from a hydroxyl group, hydrogen, alkoxy group, halogen group, carboxyl group, amino group and siloxy group, and when (4-n) is greater than 1, each of the groups X may be the same or different; are hydrolyzed to produce one or more compounds (B) selected from the group of compounds represented by the following general

formula (II):



Formula (II)

- 5 wherein m represents an integer from 1 to 4; n represents an integer from 0 to 3; $m+n \leq 4$; R represents an organic group in which a carbon atom is directly connected to a silicone atom, and when n is greater than 1, each of the R groups may be the same or different; and Y represents at least one group selected from an alkoxy group, hydrogen and siloxy group, and when $(4-m-n)$ is greater than 1, each of the groups Y may be the same or different; provided that compound (B) comprises at least one compound of formula (II) wherein $m=2$ or 3 and at least one of the R groups thereof
10 possess affinity for at least one of a continuous phase and a dispersed phase; and compound (B) is polycondensed to synthesize organopolysiloxane constituting a capsule wall. The present invention was thus completed.
[0011] The term "continuous phase" and "dispersed phase" usually represent a dispersing medium and a dispersed phase before formation of a wall of a microcapsule respectively. In this specification, an outer phase and an inner phase after formation of a wall of a microcapsule are also called and referred to as "continuous phase" and "dispersed phase",
15 respectively.
[0012] According to the present invention the organopolysiloxane constituting a wall of a microcapsule can be synthesized directly from compound (B) belonging to the so-called hydroxysilanes. Further, the above-described organopolysiloxane can constitute a capsule wall necessary for producing a microcapsule containing core material, thus not requiring formation of a capsule wall by a conventional coacervation method.
20 [0013] The present invention provides a microcapsule containing core material and a capsule wall, in which the capsule wall of the microcapsule comprises: an organopolysiloxane synthesized by polycondensing a compound (B), monomer or monomeric mixture, wherein compound (B) contains one or more compounds represented by the general formula (II) as defined above. The present invention further provides a method for producing a microcapsule containing core material which comprises a process wherein compound (B) is polycondensed to synthesize organopolysiloxane
25 and form the capsule wall.
[0014] Compound (B), which is used for producing a microcapsule having a core material encapsulated therein, as provided by the present invention, is usually obtained by hydrolyzing a compound (A), monomer or monomeric mixture, wherein compound (A) contains one or more compounds represented by the following general formula (I) as defined above, provided that compound (A) contains at least one compound of formula (I) having an R group which possesses
30 affinity for at least one of a continuous phase and a dispersed phase.
[0015] In the present invention, the term "microcapsule" means a capsule such as a microcapsule or nanocapsule, and thus has a broad meaning in comparison with the typical narrower meaning of the term "microcapsule". For example, in general, a "microcapsule" in a narrow sense means a capsule having a particle size of 1 μm to 1 mm and a "nanocapsule" means a capsule having a particle size less than 1 μm . As such, unless otherwise mentioned herein, the term "microcapsule" means a microcapsule in its broad sense in this specification and includes both microcapsules and nanocapsules. The phrase "microcapsule containing core material" means a microcapsule containing core material in the hollow space formed by a capsule wall.
35 [0016] Compound (B) is a compound or a group of two or more compounds selected from those represented by the general formula (II). At least one compound constituting compound (B) is represented by the general formula (II)
40 wherein $m=2$ or 3. At least one compound constituting the compound (B) is a compound having at least one R group which possess affinity for at least one of a continuous phase and a dispersed phase.
[0017] The capsule wall of the microcapsule containing core material of the present invention is formed by polycondensing compound (B) to synthesize an organopolysiloxane.
[0018] Condensation of compound (B) is a reaction in which a -SiOH group in the general formula (II) is reacted with
45 -SiL- (wherein, L represents a leaving group such as a hydroxyl group and the like) in another molecule constituting compound (B) or another prepolymer to form an -SiOSi- linkage. By this condensation reaction, organopolysiloxane is formed which constitutes a capsule wall.
[0019] As explained below, in the production of a microcapsule containing core material of the present invention, condensation of compound (B) is conducted to a certain extent to prepare a prepolymer of compound (B) before the formation of organopolysiloxane, which constitutes a capsule wall. Therefore, the prepolymer is also constituted by organopolysiloxane formed by the condensation reaction.
50 [0020] The formulation of the organopolysiloxane which is formed as described above and constitutes the capsule wall in the present invention or a prepolymer is represented by the following general formula:



wherein, R represents an organic group in which a carbon atom is directly connected with a silicon atom, or represents hydrogen and when two or more R groups are present, they may be the same or different; h, i, j, k represents 0 or a

positive integer; R' represents an alkyl group or hydrogen; p represents 0 or a positive integer; and $0 \leq h+p \leq j+2k+2$.

[0021] As described above, if two or more R groups are connected to one silicon atom in the general formula (III), the R groups may be the same or different each other. The formulations shown in parentheses directly before subscripts h, i, j may all be the same or different. For example, the R groups in $(R_2SiO_{1/2})_h$ may all be the same or different.

[0022] The organopolysiloxane constituting a prepolymer grows to be a larger polymer constituting a capsule wall, by way of condensation reaction of SiOH on a prepolymer with SiL (wherein, L represents a leaving group such as a hydroxyl group and the like) on another prepolymer. Therefore, although both organopolysiloxane constituting a capsule wall and organopolysiloxane constituting a prepolymer are represented by the above-described general formula (III), the values of h, i, j, k and p in the general formula (III) are different in the prepolymer and the capsule wall. Namely, when the above-described general formula (III) represents an organopolysiloxane constituting a capsule wall, at least one of i and j is such a positive integer that a polymer sufficient to form a microcapsule is obtained. When the above-described general formula (III) represents organopolysiloxane constituting Prepolymer, h, i, j and k represent 0 or a positive integer that is smaller than the h, i, j and k when the above-described general formula (III) represents the organopolysiloxane constituting a capsule wall. The value of p depends on the extent of hydrolysis of the compound (B) obtained by hydrolysis of the compound (A), and the extent of condensation reaction of the compound (B). It is in the range wherein the organopolysiloxane constituting a prepolymer and a capsule wall is sufficiently formed.

[0023] In an organopolysiloxane synthesized by polycondensation of compound (B), an alkoxy group or a hydroxyl group may partially remain on a silicon atom, or none of them may remain at all.

[0024] Compound (B) used for producing the microcapsule of the present invention having a core material therein is obtained by hydrolysis of compound (A). Compound (A) is a compound or a group of two or more compounds selected from compounds represented by the general formula (I).

[0025] The method for producing the microcapsule containing core materials of the present invention include processes using the following steps in order:

- 25 "(1) producing compound (B) by hydrolysis of compound (A)",
- "(2) Polycondensing by neutralizing of compound (B)
- "(3) Mixing and emulsifying with a core material and/or a second liquid phase", and
- "(4) Curing treatment".

[0026] Further to the above steps, an "Over coat treatment", mentioned below or a "Surface treatment by the compound (A)" (hereinafter, abbreviated as "Surface treatment") may also be carried out before the "Curing treatment" step, if necessary or desired.

[0027] Examples of compound (A) used in the production method of the present invention include a compound or a group of compounds carrying a hydrophilic group, a compound or a group of compounds carrying a hydrophobic group, a compound or a group of compounds carrying a group having affinity with a fluorocarbon, tetraalkoxysilane, a compound or a group of compounds carrying an amphiphatic group and a compound or a group of compounds carrying a surface active group.

[0028] The term "amphiphatic" as used herein refers to means having affinity against both of two media, which can not mix with each other, and the amphiphatic group is a group carrying both groups having mutually different affinities such as a hydrophilic group and a hydrophobic group.

[0029] Compound (A) used in the production method of the present invention may be composed of one kind of compound and/or one kind of group of compounds or be composed of a combination of several kinds of compounds and/or several kinds of groups of compounds. For example, compound (A) may be composed of a compound carrying a hydrophilic group and a compound carrying a hydrophobic group.

[0030] The kind of compound (A), and the proportion of several kinds of compounds and/or several kinds of groups of compounds, when compound (A) is composed of several kinds of compounds and/or several kinds of groups of compounds, is preferably selected so that a prepolymer formed by condensation of compound (B) obtained by hydrolysis of compound (A) possess affinity with at least one of a continuous phase and dispersed phase, and the prepolymer formed is dispersed steadily.

[0031] In a compound carrying a hydrophilic group which composes compound (A), it is preferable that the R group in the general formula (I) carries a hydrophilic group, and the R group carrying a hydrophilic group is connected to a silicon atom. Two or more R groups carrying a hydrophilic group may be connected to one silicon atom. When a plurality of hydrophilic groups are connected to one R group, the plurality of hydrophilic groups may include two or more kinds of hydrophilic groups. In addition to a hydrophilic group, a hydrophobic group and a group having affinity with a fluorocarbon may be connected to R group carrying a hydrophilic group.

[0032] Examples of a compound which derives a hydrophilic group in compound (A) include polyethers such as a polyoxyethylene, polyoxypropylene and polyoxyethylene-polyoxypropylene copolymer, saccharides including polysaccharides and monosaccharides such as pullulan, sorbitol, chitin and chitosan or amino sugars, proteins, antibodies,

- hydrolyzed protein, polyamino acids, carboxylic acids or salts and derivatives thereof, polycarboxylic acids or salts and derivatives thereof, sulfuric acid or salts and derivatives thereof, phosphoric acid or salts and derivatives thereof, sulfonic acid or salts and derivatives thereof, phosphonic acid or salts and derivatives thereof, quaternary ammonium groups, amine or salts thereof and polyamines or salts thereof. The compound which derives a hydrophilic group in the compound (A) is not limited to the above-exemplified compounds. As a group which is connected with the above-exemplified hydrophilic group to form hydrophilic group "R", -CH₂-, -(CH₂)₂-, -(CH₂)₃-, -(CH₂)₃OCH₂CH(OH)CH₂-, -(CH₂)₃NHCO-, -(CH₂)₃CH(CH₂COOH)CO- and -(CH₂)₃CH(COOH)CH₂CO- are exemplified, and a silicon atom is connected to the left side of this partial structural formula and the above-described hydrophilic group is connected to the right side of the formula.
- [0033] Specific examples of a compound carrying a hydrophilic group and composing compound (A) include polyoxyethylene-modified silicones [for example, KF-354 (trade name)] carrying, as a hydrophilic group, a polyether such as a polyoxyethylene, polyoxypropylene and polyoxyethylene-polyoxypropylene copolymer, polyethoxypropyltrimethoxysilanes [for example, KBM-641 (trade name) manufactured by Shin-Etsu Chemical Co., Ltd.], N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed protein derived from γ -glycidoxypropytriethoxysilane and hydroxylized protein, N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed protein derived from γ -glycidoxypropylmethyldiethoxysilane and hydroxylized protein (JP-A-8-67608), and compounds derived from the hydrophilic substance carrying a hydrophilic group as described above and a silane coupling agent such as β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -[N-(β -aminoethyl)amino]propylmethyldimethoxysilane, γ -[N-(β -aminoethyl)amino]propyltrimethoxysilane, γ -[N-(β -aminoethyl)amino]propyltriethoxysilane, γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, γ -(N-phenylamino)propyltrimethoxysilane, γ -chloropropyltrimethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -isocyanate propyltriethoxysilane and 3-triethoxysilylpropylsuccinic anhydride. The compound carrying a hydrophilic group and composing compound (A) is not limited to the above-described examples.
- [0034] Regarding the above-described polyethers such as a polyoxyethylene, polyoxypropylene and polyoxyethylene-polyoxypropylene copolymer, it is preferable that the number-average polymerization degree of oxyethylene and oxypropylene is from 1 to 2000, particularly from 4 to 800.
- [0035] Preferable examples of the hydrolyzed protein in the above-described N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed protein and N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed protein include, but are not limited to, hydrolysates of animal-derived protein such as collagen, elastin, keratin, fibroin (silk), sericin (silk), casein and conchiolin, vegetable-derived protein such as wheat protein, soybean protein, sesame protein and zein (corn protein), and microorganism-derived protein such as yeast protein. It is preferable that the number-average molecular weight of the hydrolyzed protein is from about 100 to 50000, particularly from about 200 to 5000.
- [0036] In a compound carrying a hydrophobic group which composes compound (A), it is preferable that the R group in the general formula (I) carries a hydrophobic group and the R group carrying a hydrophobic group is connected to a silicon atom. Two or more R groups carrying a hydrophobic group may be connected to one silicon atom, and a plurality of hydrophobic groups are connected to one R group. The plurality of hydrophilic groups may include two or more kinds of hydrophobic groups. In addition to a hydrophobic group, a group having affinity with a fluorocarbon may be connected to an R group carrying a hydrophobic group.
- [0037] Examples of the hydrophobic group include a straight-chain hydrocarbon, branched hydrocarbon, unsaturated hydrocarbon, aromatic compounds and esters.
- [0038] It is preferable that one or more of these functional groups are connected to R, although the hydrophobic group is not limited to the above-exemplified compounds.
- [0039] Specific examples of a compound carrying a hydrophobic group and composing compound (A) include methyltrimethoxysilane, methyl dichlorosilane, methyl trimethoxysilane, methyl triethoxysilane, methyl trichlorosilane, dimethyltrimethoxysilane, dimethyl diethoxysilane, dimethyl dichlorosilane, phenyl trimethoxysilane, phenyl triethoxysilane, phenyl trichlorosilane, diphenyl dimethoxysilane, diphenyl diethoxysilane, diphenyl dichlorosilane, hexyl trimethoxysilane, octyl triethoxysilane, decyl trimethoxysilane, stearoxypropyl trimethoxysilane, vinyl trimethoxysilane, vinyl triethoxysilane, vinyl tris-(β -methoxyethoxy) silane, vinyl trichlorosilane, γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -methacryloxypropylmethyl diethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -glycidoxypropytriethoxysilane, γ -glycidoxypropylmethyldiethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -[N-(β -aminoethyl)amino]propylmethyldimethoxysilane, γ -[N-(β -aminoethyl)amino]propyltriethoxysilane, γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, γ -(N-phenylamino)propyltrimethoxysilane, γ -chloropropyltrimethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -isocyanatepropyltriethoxysilane and 3-triethoxysilylpropylsuccinic anhydride. Further, as

specific examples of the compound represented by the general formula (I) in which X is a siloxy group, octamethylcyclotetrasiloxane, dihydrogenhexamethylcyclotetrasiloxane and trihydrogenpentamethylcyclotetrasiloxane are listed. The compound carrying a hydrophobic group and composed of the compounds (A) is not limited to the above exemplified compounds.

- 5 [0040] In the compound carrying a group having affinity with a fluorocarbon, it is preferable that the R group in the general formula (I) carries a group having affinity with a fluorocarbon, and the R group carrying a group having affinity with a fluorocarbon is connected to one silicon atom. Two or more R groups carrying a group having affinity with a fluorocarbon may be connected to one silicon atom, and a plurality of groups having affinity with a fluorocarbon may be connected to the R group. The plurality of groups having affinity with a fluorocarbon may include two or more kinds of groups having affinity with a fluorocarbon.

10 [0041] Examples of the compound carrying a group having affinity with a fluorocarbon and composing compounds (A) include $C_8F_{17}CH_2CH_2Si(OCH_3)_3$, $CF_3CH_2CH_2Si(OCH_3)_3$, and compounds derived from a substance having affinity with a fluorocarbon and a silane coupling agent such as vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(β -methoxyethoxy)silane, vinyltrichlorosilane, γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldiethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -glycidoxypropylmethyltriethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -[N-(β -aminoethyl)amino]propylmethyldimethoxysilane, γ -[N-(β -aminoethyl)amino]propyltrimethoxysilane, γ -[N-(β -aminoethyl)amino]propyltriethoxysilane, γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, γ -(N-phenylamino)propyltrimethoxysilane, γ -chloropropyltrimethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -

15 20 isocyanatepropyltriethoxysilane and 3-triethoxysilylpropylsuccinic anhydride. The compound carrying a group having affinity with a fluorocarbon and composing compound (A) is not limited to the above exemplified compounds.

[0042] As specific examples of the compound having both a hydrophilic group and a hydrophobic group, which composes compound (A), a compound which generates N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed protein by hydrolyzing the substituents such as an alkoxy group and the like are exemplified.

25 [0043] When the microcapsule containing core material, made from compound (A), is dispersed in water or hydrophilic continuous phase, compound (A) is as follows.

[0044] When a hydrophilic group in compound (A) is a polyether such as a polyoxyethylene, polyoxypropylene and polyoxyethylene-polyoxypropylene copolymer, it is preferable that total number-average polymerization degree of oxyethylene and oxypropylene is from 10 to 1000, particularly from about 20 to 400. When compound (A) is a hydrolyzed protein, it is preferable that the number-average molecular weight thereof is from 200 to 50000, particularly from about 400 to 5000.

[0045] It is preferable that the molar ratio of a compound (A) carrying a hydrophilic group (including the case wherein the R group carries a hydrophilic group and a hydrophobic group together) to a compound (A) carrying a hydrophobic group is from about 1:0 to 1:1000, particularly from about 1:2 to 1:200, in terms of monomers.

30 35 [0046] When a monomethyl type compound, wherein only one R group in the formula (I) is a methyl group, is used as compound (A) carrying a hydrophobic group, it is preferable that at least one compound selected from methyltriethoxysilane methyltrimethoxysilane and methyltrichlorosilane is used, or that such a compound is used in combination with at least one compound selected from the group consisting of dimethylmethoxysilane, dimethyldimethoxysilane, dimethyldichlorosilane, octamethylcyclotetrasiloxane, phenyltriethoxysilane, hexyltrimethoxysilane, octyltriethoxysilane, decyltrimethoxysilane and stearoxypropyltrimethoxysilane. The molar ratio of the monomethyl type compound to another compound carrying a hydrophobic group may be from 100:0 to 0:100, but it is preferable that the molar ratio is from about 100:3 to 100:80, in terms of monomers. The monomethyl type compound and the other compounds carrying a hydrophobic group are not limited to the above-exemplified compounds.

40 45 [0047] When the microcapsule containing core material is made from compound (A), and is dispersed in a hydrophobic continuous phase or non-aqueous continuous phase, compound (A) is as follows.

[0048] When a hydrophilic group in compound (A) is a polyether such as a polyoxyethylene, polyoxypropylene and polyoxyethylene-polyoxypropylene copolymer, it is preferable that total number-average polymerization degree of oxyethylene and oxypropylene is from 3 to 20, particularly from 5 to 10. When compound (A) is a hydrolyzed protein, it is preferable that the number-average molecular weight thereof is from about 100 to 2000, particularly from about 200 to 1000.

50 55 [0049] When a monomethyl type compound wherein only one R group in formula (I) is a methyl group is used as compound (A) carrying a hydrophobic group, it is preferable that at least one compound selected from methyltriethoxysilane, methyltrimethoxysilane and methyltrichlorosilane is used, or such a compound is used in combination with at least one compound selected from dimethylmethoxysilane, dimethyldimethoxysilane, dimethyldichlorosilane, octamethylcyclotetrasiloxane, phenyltriethoxysilane, hexyltrimethoxysilane, octyltriethoxysilane, decyltrimethoxysilane and stearoxypropyltrimethoxysilane. The molar ratio of the monomethyl type compound to another compound carrying a hydrophobic group may be from 100:0 to 0:100, but it is preferable that the molar ratio is from about 10:100 to 80:100, in terms of monomers. The monomethyl type compound and the other compounds carrying a hydrophobic group are

- not limited to the above-exemplified compounds.
- [0050] Hydrolysis of compound (A) will be described below.
- [0051] Compound (B) is usually obtained by hydrolysis of compound (A). As a medium for this hydrolysis, water is usually used. In addition, a small amount of an organic solvent soluble in water, salts, protein modifying agent such as 5 urea, and the like may also be added to water. Addition of these additives is effective when neutralization after hydrolysis of compound (A) or emulsification by mixing with a second liquid phase are conducted at a temperature of not more than 0°C, and is one preferable method. Further, in a process from hydrolysis of compound (A) to production of a pre-polymer via compound (B), it is preferable to use a medium having a viscosity of 10 to 2000 mPa · s before addition of compound (A), to control reaction speed so that the condensation reaction rate does not rise so much, to prevent dep-10 osition following insolubilization of the prepolymer, and to stabilize the solution. As a thickening substance for preparing a medium having a viscosity of 10 to 2000 mPa · s, polyvinyl alcohol, polyacrylamide, carboxymethylcellulose sodium, carboxymethylxanthan, hydroxyethylcellulose, carageenan, chitin, chitosan, polypeptide, gelatin and sericin are exemplified. In particular, an aqueous gelatin solution having a viscosity of 10 to 2000 mPa · s is exemplified.
- [0052] It is preferable that the hydrolysis of compound (A) is conducted at a temperature from -5°C to 90°C, particu-15 larly from 5°C to 75°C, with complete stirring (i.e. under stirring conditions).
- [0053] The hydrolysis of compound (A) may be conducted at either an acidic pH or a basic pH. Selection of these properties depends on the nature of the compound (A).
- [0054] When the hydrolysis of compound (A) is conducted at an acidic pH, it is preferably conducted at pH 1 - 5, particu-20 larly of 2 - 4. When acidity in hydrolysis is too strong, a core material may not be later incorporated thereto sufficiently, and a hyaline substance may be partially produced, though it depends also on the constitution and concentration of compound (A). Examples of the acid to be used include an organic acid such as acetic acid, and an inorganic acid such as hydrochloric acid, sulfuric acid, and phosphoric acid. Particularly, when compound (A) carries a hydrophilic group which is a hydrolyzate of an animal-derived protein such as collagen, elastin, keratin, fibroin (silk), sericin (silk), casein and conchiolin, if the hydrolysis of compound (A) is conducted at an acidic pH, preferable results 25 are obtained for obtaining a microcapsule containing core material.
- [0055] When the hydrolysis is conducted at a basic pH, it is preferably conducted at a pH of 7.5 to 11.5, particularly of 8 to 10. When basicity in hydrolysis is too strong, a core material may not be later incorporated therein sufficiently, and a hyaline substance may be partially produced, though it depends also on the constitution and concentration of compound (A). As the alkali to be used, for example, sodium hydroxide and potassium hydroxide are listed. Particularly, 30 when compound (A) carries a hydrophilic group which is a hydrolyzate of vegetable-derived protein such as for example wheat protein, soybean protein and sesame protein, if the hydrolysis of compound (A) is conducted at a basic pH, preferable results are obtained for obtaining a microcapsule containing core material.
- [0056] Compound (B) produced by hydrolysis of compound (A) is polycondensed usually by neutralization.
- [0057] The neutralization is preferably conducted at a temperature from -30°C to 80°C, particularly from -5°C to 55°C 35 with sufficient stirring. As acids and alkalis used for the neutralization, the same compounds as those listed for the above-described hydrolysis are exemplified. As the medium for the neutralization, water is exemplified.
- [0058] In the production method of the present invention, production of compound (B) and polycondensation by neutralization are conducted to a certain extent before mixing and emulsification with a core material and/or second liquid phase, in order to prepare a prepolymer of compound (B) previously. When at least one compound (B) which carries at 40 least one hydrophilic R, particularly, carries at least one polypeptide having a number-average molecular weight of about 100 to 50000, as R, or a polyoxyethylene having a number-average polymerization degree of 1 to 2000, as R, is used, this method is particularly preferable since the prepolymer can be stabilized in this method.
- [0059] Extent of the polycondensation of compound (B) by neutralization to be conducted before mixing and emulsification with a core material and/or second liquid phase may be changed according to the other conditions as long as 45 the formed prepolymer is stable. In other words, mixing and emulsification with a core material and/or second liquid phase must be conducted before the formed prepolymer become unstable.
- [0060] When the prepolymer is unstable and easily precipitated, a method for preparing a prepolymer by hydrolysis of compound (A) in a viscous solution such as an aqueous gelatin solution is preferable since the prepolymer can be stabilized in this method.
- [0061] It is preferable that after preparation of the prepolymer, this prepolymer in an aqueous solvent is mixed with a 50 hydrophobic substance and/or a non-aqueous solvent to prepare an emulsion.
- [0062] In the above-described method, after mixing of a hydrophobic substance and/or a non-aqueous solvent, the prepolymer causes mutual condensation and grows to a larger polymer to become organopolysiloxane constituting a capsule wall.
- [0063] Then, mixing and emulsification with a core material and/or second liquid phase is utilized as described below.
- [0064] The following methods are exemplified methods for mixing and emulsification with a core material and/or sec-55 ond liquid phase:
- [0065] In the case of a microcapsule containing core material dispersed in water or a hydrophilic dispersing medium,

a method in which a prepolymer is prepared in an aqueous dispersing medium, then, a core material in the form of liquid (second liquid phase) alone, or a core material and a solvent thereof (second liquid phase), is added.

[0066] In the case of a microcapsule containing core material dispersed in a hydrophobic dispersing medium or a non-aqueous dispersing medium, when the core material is soluble in an aqueous solvent or is hydrophilic, a method in which, to an aqueous solvent dispersion of a prepolymer, the core material is added as it is, or after being dissolved in an aqueous solvent, and the resulted liquid is mixed with a solvent immiscible with the aqueous solvent (continuous phase in the second liquid phase) to invert the phase and emulsify. The core material may be added after the inversion of the phase and emulsification thereof.

[0067] In the method of the present invention, since a core material can be incorporated at neutral condition, a micro-capsule containing a substance unstable at conditions other than neutral can be produced. Mixing and emulsification with a core material and/or second phase are usually conducted at from -30°C to 95°C, particularly from -5°C to 60°C. Examples of the core material utilized are provided below.

[0068] Examples of the core material utilized include water, fatty acids particularly higher fatty acid, hydrocarbons, organic solvents, esters, phenols, silicones, silanes, metal alkoxides, alcohols particularly higher alcohol, animal and vegetable oils, extracted components, electrodonative coloration organic compounds, coloring matters, ultraviolet ray absorbers, vitamins, effective drug components, aroma components, preservative, sterilizer, salts; amino acid and its derivatives, protein, hydrolyzed protein and its derivatives, saccharides, polysaccharide, enzymes and fluorocarbon-like substances.

[0069] The core material is not limited to the above-exemplified substances.

[0070] Examples of the higher fatty acids include capric acid, lauric acid, miristic acid, palmitic acid, stearic acid, behenic acid, 12-hydroxystearic acid, undecylenic acid, lanolin fatty acid, isostearic acid, linoleic acid, oleic acid, linolenic acid, arachidonic acid, eicosapentaenic acid and docosahexaenic acid.

[0071] Examples of the hydrocarbons include liquid paraffin, isoparaffin, ozokerite, pristan, ceresin, vaseline and microcrystalline wax.

[0072] Examples of the organic solvent include hexane, heptane, octane, benzene, toluene, xylene, chlorobenzene, ethyl acetate and butyl acetate.

[0073] Examples of the esters include isopropyl miristate, cetyl octanoate, octyldecyl miristate, isopropyl palmitate, butyl stearate, hexyl laurate, miristyl miristate, decyl oleate, hexyldecyl dimethyloctanoate, cetyl lactate, miristyl lactate, lanolin lactate, methyl isostearate, isooctyl stearate, cholesteryl 12-hydroxystearate, ethylene glycol di-2-ethylhexylate, dipentaerythrithol fatty ester, n-alkyl glycol monoisostearate, propylene glycol dicaprate, neopentyl glycol dicaprate, glycetyl tricaprate, isostearyl neopentanoate, diisostearyl malate, glycetyl monostearate, glycetyl distearate, glycetyl di-2-heptylundecanoate, trimethylolpropane tri-2-ethylhexanoate, trimethylolpropane triisostearate, neopentyl glycol di-2-ethylhexanoate, pentaerythritol tetra-2-ethylhexanoate, glycetyl tri-2-ethylhexanoate, cetyl 2-ethylhexanoate, 2-ethylhexyl isononanoate, isononyl isononanoate, isodecyl isononanoate, isotridecyl isononanoate, 2-ethylhexyl palmitate, glycetyl trimiristate, glycetyl trioctanoate, glycetyl triisopalmitate, castor oil fatty acid methyl ester, oleyl oleate, glycetyl acetate, 2-heptylundecyl palmitate, diisopropyl adipate, diisobutyl adipate, N-lauroyl-L-glutamic acid-2-octyldecyl ester, 2-heptylundecyl adipate, ethyl laurate, di-2-ethylhexyl sebacate, 2-hexyldecyl miristate, 2-hexyldecyl palmitate, 2-hexyldecyl adipate, 2-hexyldecyl succinate and diisopropyl sebacate.

[0074] Examples of the phenols include t-butylphenol, nonylphenol, dodecylphenol, α-naphthol, β-naphthol, hydroquinone monomethyl ether, p-chlorophenol, p-bromophenol, o-phenylphenol, p-phenylphenol, methyl p-hydroxybenzoate, ethyl p-hydroxybenzoate, propyl p-hydroxybenzoate, 3-isopropylcatechol, p-t-butylcatechol, 4,4'-methylenediphenol, bisphenol A, 1,2-dihydroxynaphthalene, chlorocatechol, bromocatechol, 2,4-dihydroxybenzophenone, phenolphthalein, methyl gallate, ethyl gallate, propyl gallate, hexyl gallate, octyl gallate, dodecyl gallate, cetyl gallate, stearyl gallate, tannic acid, phenol resin, zinc salicylate and zinc t-butylsalicylate.

[0075] Examples of the silicones include dimethylpolysiloxane, methylphenylpolysiloxane, dimethylsiloxane-methylstearoxysiloxane copolymer, dimethylsiloxane-methylmethoxysiloxane copolymer, dimethylsiloxane-methylethoxysiloxane copolymer, trimethylsiloxysilicic acid, methylcyclopolsioxane, methylhydrogenpolysiloxane, high polymer methylpolysiloxane and crosslinked-type methylpolysiloxane.

[0076] Examples of the silanes include methyltrimethoxysilane, methyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, hexyltrimethoxysilane, octyltrimethoxysilane, decyltrimethoxysilane, tetramethoxysilane, tetraethoxysilane and the like.

[0077] Examples of the metal alkoxides include trimethyl borate, triethyl borate, tetraethyl titanate and tetraisopropyl titanate.

[0078] Examples of the higher alcohols include capryl alcohol, lauryl alcohol, miristyl alcohol, cetyl alcohol, stearyl alcohol, arachyl alcohol, behenyl alcohol, oleyl alcohol, ketostearyl alcohol, monostearyl glycetyl ether, 2-decyldodecanol, 2-hexyldecanol, 2-hexylundecanol, 2-octylundecanol, 2-heptylundecanol, lanolin alcohol, cholesterol, phytosterol and isostearyl alcohol.

[0079] Examples of the animal and vegetable oils include avocado oil, tsubaki oil, macadamia nut oil, corn oil, olive

oil, evening primrose oil, rapeseed oil, yolk oil, sesame oil, persic oil, wheat germ oil, camellia sasanqua oil, castor oil, curing castor oil, linseed oil, safflower oil, cotton seed oil, curing cotton seed oil, soybean oil, curing soybean oil, peanut oil, tee nip oil, Japanese Nutmeg oil, rice bran oil, chinese tung oil, japanese tung oil, cinnamon oil, jojoba oil, germ oil, almond oil, cocoa oil, palm oil, curing palm oil, horse tallow, turtle oil, mink oil, squalane, squalene, orange roughy oil, 5 beef tallow, curing beef oil, beef bone oil, neat's foot oil, mutton oil, lard, train oil, curing train oil, fishoil, curing fish oil, lanolin, lanolin alcohol, hydrogenater lanolin, lanolin acetate, liquid lanolin, lanolin fatty acid isopropyl ester, cholestryl lanonate, cyclic lanolin, polyoxyethylenelanolin alcohol ether, polyoxyethylenelanolin alcohol acetate, polyethylene glycol lanolin fatty acid, polyoxyethylene hydrogenater lanolin alcohol ether, carnauba wax, candelilla wax, jojoba wax, hard lanolin, Japan wax, indian millet wax, cotton wax, wax myrtle, insect wax, montan wax, rice bean wax, shellac wax, 10 jojoba wax, bee wax, train wax, jojoba alcohol, abietic acid and hydrogenated abietic acid.

[0080] Examples of the electrodonative coloration organic compound include diarylphtthalides, polyaryl carbinols, leuco auramines, acyl auramines, aryl auramines, rhodamine- β -lactams, indolines, spiropyrans, fluorans and the like. Specific examples thereof include crystal violet lactone, malachite green lactone, Michler's hydrol, crytal violet carbinol, 15 malachite green carbinol, N-(2,3-dichlorophenyl)leuco auramine, N-benzoyl auramine, N-acetyl auramine, N-phenyl auramine, rhodamine- β -lactam, 2-(phenyliminoethanediidene)-3,3-dimethylindoline, N-3,3-trimethylindolinobenzspiro-lane, 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-7-methoxyfluoran, 3-diethylamino-6-benzyloxyfluoran and 1, 2-benz-6 diethylaminofluoran.

[0081] Examples of the coloring matters include colorless white pigments such as titanium dioxide, zinc oxide and the like, inorganic red pigments such as iron oxide (red iron oxide) and iron titanate, inorganic brown pigments such as γ -iron oxide, inorganic yellow pigments such as yellow iron oxide and loess, inorganic black pigments such as black iron oxide, carbon black and lower titanium oxide, inorganic violet pigments such as mango violet and cobalt violet, inorganic green pigments such as chromium oxide, chromium hydroxide and cobalt titanate, inorganic blue pigments such as ultramarine and iron blue, organic dyes such as Red 201, Red 202, Red 204, Red 205, Red 218, Red 220, Red 225, Red 226, Red 228, Red 405, Orange 201, Orange 203, Orange 204, Yellow 401, Green 202 and Blue 404, organic pigments of zirconium, barium or aluminum lake, such as Red 3, Red 104, Red 106, Red 227, Red 230, Red 401, Red 505, Orange 205, Yellow 4, Yellow 5, Yellow 202, Yellow 203, Green 3, Violet 201 and Blue 11, natural pigments such as chlorophyll and β -carotene, mica titanium, red iron oxide-treated mica titanium, yellow iron oxide-treated mica titanium, black iron oxide-treated mica titanium, iron oxide- yellow iron oxide-treated mica titanium, ultramarine-treated mica titanium, carmine-treated mica titanium, chromium oxide-treated mica titanium and carbon black-treated mica titanium. Further, examples thereof include talc, kaolin, mica, phlogopite, sericite, white mica, synthetic mica, epidolite, lithia mica, vermiculite, inorganic powders such as apatite fluoride, hydroxyapatite, ceramic powder, metal soap (zinc miristate, calcium palmitate, aluminum stearate and the like), boron nitride, silica-alumina, silica-magnesia, bentonite, fuller's earth, Japanese acid clay, active white earth, montmorillonite and attapulgite; and organic powder such as a 30 polyamide resin powder (nylon powder), polyethylene powder, polymethyl methacrylate powder, polystyrene powder, styrene-acrylic acid copolymer resin powder, benzoguanamine resin powder, polyethylene tetrafluoride powder and cellulose powder.

[0082] Examples of the ultraviolet ray absorbers include salicylic acid-based ultraviolet ray absorbers such as phenyl salicylate, p-t-butylphenyl salicylate and p-octylphenyl salicylate, benzophenone-based ultraviolet ray absorbers or derivatives thereof such as 2,4-dihydroxybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octyloxybenzophenone, 2-hydroxy-4-dodecyloxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone and 2-hydroxy-4-methoxy-5-sulfobenzophenone, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-5'-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-3',5'-di-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-3'-t-butyl-5'-methylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-t-butylphenyl)-5-chlorobenzotriazole, 2-(2'-hydroxy-3',5'-di-t-amylphenyl)benzotriazole, 2-[2'-hydroxy-3'-(3",4",5",6"-tetrahydrophthalimidemethyl)-5'-methylphenyl]-benzotriazole, 2-(2'-hydroxyl-3'-dodecyl-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-3'-undecyl-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-3'-tridecyl-5'-methylphenyl)benzotriazole, 2-[2'-hydroxy-4'-(2"-ethylhexyl)oxyphenyl]benzotriazole, 2-[2'-hydroxy-4'-(2"-ethyloctyl)oxyphenyl]benzotriazole, 2-[2'-hydroxy-4'-(2"-propyloctyl)oxyphenyl]benzotriazole, 2-[2'-hydroxy-4'-(2"-propylheptyl)oxyphenyl]benzotriazole, 2-[2'-hydroxy-4'-(2"-propylhexyl)oxyphenyl]benzotriazole, 2-[2'-hydroxy-4'(1"-ethylhexyl)oxyphenyl]benzotriazole, 2-[2'-hydroxy-4'(1"-ethylheptyl)oxyphenyl]benzotriazole, 2-[2'-hydroxy-4'(1"-propylheptyl)oxyphenyl]benzotriazole, 2-[2'-hydroxy-4'(1"-propylhexyl)oxyphenyl]benzotriazole, condensate of methyl-3-(3-t-butyl-5-(2H-benzotriazole-2-yl)-4-hydroxyphenyl)propionate with polyethylene glycol (molecular weight : about 300), derivatives or ester of p-methoxycinnamic acid such as 2-ethylhexyl p-methoxycinnamate, derivatives or ester of p-dimethylaminobenzoic acid such as 2-ethylhexyl p-dimethylaminobenzoate, derivatives or ester 55 of cinnamic acid such as benzyl cinnamate, derivatives of anthranilate, salicylate and benzoaxazole, 2,4,6-tri-(p-anilino)-1-(carboxy-2'-ethylhexyl)-1,3,5-triazine, derivatives of dibenzoylmethane such as 4-t-butyl-4'-methoxydibenzoylmethane and 4-isopropyldibenzoylmethane, franone derivatives, ferulic acid or esters thereof and γ -oryzanol.

[0083] Examples of the vitamins include vitamins or derivatives thereof such as vitamin A, vitamin B, vitamin C, vita-

min D, Vitamin E, thiamine hydrochloride, pyridoxine hydrochloride, calcium pantothenate, bisbentiamine and methyl-methioninesulfonium chloride. Specifically, magnesium L-ascorbyl-2-phosphate, sodium L-ascorbyl-2-phosphate and tocopherol acetate are exemplified.

[0084] Examples of the effective drug components include sulfur drugs such as sulfamethomidine, circulatory drugs such as calcium hobatate, papaverine hydrochloride, diltiazem hydrochloride and reserpine, breathing promoting drugs such as trimetoxynol hydrochloride, bromhexine hydrochloride and tipeptidine hibenzate, antitussive expectoration drugs, antibiotics such as potassium benzylpenicillinate, sodium benzylpenicillinate, potassium phenoxytmethylpenicillinate and ampicillin, carcinostatic tumor agents such as 5-fluorourasil, N-(2-tetrahydrofuryl)-5-fluorourasil and bleomycin hydrochloride, treating agent such as timoepidium bromide, lidocaine hydrochloride and chlorpromazine hydrochloride, antihistamic agents such as diphenhydramine hydrochloride and chlorphenylamine maleate, antiphlogistic agent such as aspirin, quinine hydrochloride and sulpirin, bactericides such as salicylic acid, hinoki cypress, sulfur, parabenes and the like, preservatives, and in addition, photosensitive materials, cysteine or derivatives thereof, guaiaculene or derivatives thereof and glutathione or derivatives thereof.

[0085] Examples of the extracted components include oil-soluble arnica extract, aloe extract, oil-soluble dead nettle extract, matricaria extract, oil-soluble chamomile extract, oil-soluble glycyrrhiza extract, cape jasmine extract, oil-soluble mulberry extract, oil-soluble burdock extract, oil-soluble collagen extract, oil-soluble salvia extract, oil-soluble lithospermum root extract, oil-soluble linden extract, oil-soluble betula alba extract, oil-soluble field horsetail extract, oil-soluble yarrow extract, oil-soluble sage extract, Japanese green gentian extract, common thyme extract, citrus unshiu peel extract, oil-soluble juglanus regia L. extract, oil-soluble Japanese angelica root extract, oil-soluble common marigold extract, oil-soluble carrot extract, oil-soluble wild rose extract, oil-soluble loquat leaf extract, oil-soluble placental extract, oil-soluble hop extract, oil-soluble marronnier extract, oil-soluble peach leaf extract, mugwort extract, oil-soluble coix extract, lavender extract, lemon extract, orange extract, oil-soluble rosemary extract, oil-soluble royal jelly extract, green tea, Du Zhong tea or Rubus tea which contain tannins or flavonoids; and crude drugs of plant and animal origin or various salts thereof such as sophora japonica, scutellaria root and Souhakuhi extract.

[0086] Examples of the aroma components include oils having odor such as almond, anise, caraway, cassia, cedar leaf, cedar wood, cinnamon, citronella, clove, eucalyptus, geranium, grape fruit, lavender, lemon, lemon herb, rose oil, lime, orange flower (neroli oil), nutmeg, onion, garlic, orange, lignum vitae, orris, peppermint, pine, pine needle, rosemary, sandalwood, sassafras, spearmint, tyme, coffee, black tea, cherry, apple, pineapple, banana, peach and vanilla.

[0087] Examples of the salts include calcium carbonate, magnesium carbonate, magnesium silicate, calcium silicate, aluminum silicate, barium silicate, barium sulfate, strontium silicate, metal tungstate, silica, zeolite, barium sulfate, calcined calcium sulfate (baked gypsum), calcium phosphate, lithium chloride, sodium chloride, potassium chloride, ammonium chloride, lithium bromide, sodium bromide, potassium bromide, lithium iodide, sodium iodide, potassium iodide, iodine, sodium sulfate, potassium sulfate, ammonium sulfate, ammonium nitrate, lime nitrogen, lime perphosphate, baked phosphatic fertilizer and sodium phosphate.

[0088] Examples of the amino acid, protein, saccharides and the like include amino acids or peptides such as potassium aspartate, magnesium aspartate, sodium glutamate, lysine hydrochloride and glutathione, animal-derived proteins such as collagen, elastin, keratin, fibroin, sericin, casein and conchiolin, vegetable-derived proteins such as wheat protein, soybean protein and sesame protein, microorganism-derived proteins such as yeast protein or hydrolysates of such proteins, placenta extract, mucopolysaccharides and urea.

[0089] Examples of the enzyme include lipase, protease, super oxide, dismutase, lysozyme, alkaliphosphatase, amylase, pancreatic, glutathione peroxidase and catalase.

[0090] Examples of the fluorocarbon-like substance include Fomblin HC/04 (trade name), Fomblin HC/25 (trade name) and Fomblin HC/R (trade name) which are a liquid perfluoro ether which is a kind of polyoxy perfluoroalkanes manufactured by Monteflous (Milan, Italy).

[0091] One or more of the above-described compounds can be used as core materials. However, the core material is not limited to the above-exemplified compounds.

[0092] As a material of the continuous phase, a material which is liquid during the capsule preparation process is used. In the case of a microcapsule containing core material dispersed in a hydrophobic continuous phase or non-aqueous continuous phase, examples of materials of the continuous phase include higher fatty acids, hydrocarbons, organic solvents, esters, silicones, higher alcohols, animal and vegetable oils which are exemplified as the core materials. One or more materials among them are used for the materials of the continuous phase. Among organic solvents, even a material having a boiling point lower than that of water may also be used providing it can expel water from the system azeotropically.

[0093] In preparation of emulsion, when a particle is prepared of which particle size is essentially from 0.3 to 100 μ m and the median particle size is in the range from 1 to 20 μ m in a 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, it is preferable that the reaction solution is stirred at a speed from 50 to 1000 rpm, particularly from 300 to 1000 rpm.

[0094] In preparation of emulsion, when a reaction solution is stirred by a mechanical stirrer and then a particle is

prepared, of which the particle size is essentially from 0.1 to 30 μm and the median particle size is from 0.5 to 5 μm by a homomixer, it is preferable that the reaction solution is treated by the homomixer at a speed of from 1000 to 20000 rpm, particularly from 5000 to 10000 rpm.

[0095] In preparation of emulsion, when a reaction solution is stirred by a mechanical stirrer, treated by a homomixer and then a particle is prepared, of which the particle size is essentially from about 0.1 to 1 μm and the median particle size is from about 0.2 to 0.8 μm by a microfluidizer, it is also preferable that the reaction solution is treated by the microfluidizer at a speed of from about 300 to 5000 kg/cm^2 .

[0096] One object of the treatment by a homomixer and microfluidizer is to decrease the particle size. Another object is to produce a microcapsule containing core material wherein the capsule wall is not decomposed when shearing strength generated in this treatment is applied.

[0097] The treatment by a homomixer or a microfluidizer may be repeated two times or more to decrease the particle size more. When ultraviolet ray absorber is used as a core material, repeating the treatment by a homomixer or a microfluidizer often has another effect which decreases the amount of free ultraviolet ray absorber in the dispersion.

[0098] The preparation of emulsion in the presence of alcohol, particularly polyhydric alcohol such as ethylene glycol, polyethylene glycol and glycerin may be conducted in order to decrease the particle size more. When ultraviolet ray absorber is used as a core material, this method often has another effect which decreases the amount of free ultraviolet ray absorber in the dispersion.

[0099] The preparation of emulsion in ultrasonic wave may also be conducted in order to decrease the particle size more.

[0100] Next, surface treatment of a microcapsule containing core material by the compound (A) during production will be described below.

[0101] A microcapsule containing core material can be produced even if the surface treatment by the compound (A) during production of a microcapsule containing core material is not conducted. However, according to the production method of the present invention, it is guessed that a silanol group which did not participate in condensation remains on the surface of an uncured capsule immediately after emulsification. Therefore, a surface treatment with the compound (A) is preferably conducted to prevent coagulation of a microcapsule containing core material.

[0102] When the compound (A) for surface treatment is a compound which is easily hydrolyzed in water such as a chlorosilane including trimethylchlorosilane and hexamethylsilazane, it is preferable that this compound (A) is added to the emulsion solution after emulsification and then, the solution is neutralized.

[0103] When the compound (A) for surface treatment is an alkoxy silane like trimethylethoxysilane, it is necessary that following emulsification, this neutral solution is made somewhat acidic or basic and the alkoxy silane is hydrolyzed once. Also when a compound (A) carrying a silanol group from the beginning is used as it is for surface treatment, it is necessary that following emulsification, this neutral solution is made somewhat acidic or basic. Then, the compound (A) is fixed on the surface of a capsule by neutralization. The control of pH should be conducted carefully so that the capsule is not decomposed. In the case of treatment at an acidic pH, the pH is preferably from about 3 to 6.5. In the case of treatment at a basic pH, the pH is preferably from about 7.5 to 10. Examples of the compound (A) used in this surface treatment will be described below, however, it is not limited to the exemplified compounds.

[0104] One object of the surface treatment is to prevent coagulation of a microcapsule containing core material. It is preferable to add, after preparation of emulsion, a compound (A) carrying 3 alkyl groups on a silicon atom such as trimethylchlorosilane, ethoxytrimethylsilane, t-butyldimethylchlorosilane, hexamethyldisiloxane and hexamethyldisilazane to prevent coagulation of a microcapsule containing core material.

[0105] Further, after preparation of emulsion, a compound (A) carrying a cationic group as an organic substituent such as octadecyldimethyl-(3-trimethoxysilylpropyl)ammonium chloride can be added, hydrolyzed and neutralized to make the surface of a microcapsule containing core material cationic.

[0106] Further, it is possible, after preparation of emulsion, to variously modify the properties of the surface of a microcapsule containing core material and to obtain various functions by controlling pH to neutralize a compound (A) such as methyl diethoxysilane, methyl dichlorosilane, tetramethoxysilane, tetraethoxysilane, tetrachlorosilane, methyl trimethoxysilane, methyl triethoxysilane, methyl trichlorosilane, dimethyl dimethoxysilane, dimethyl diethoxysilane, dimethyl dichlorosilane, octamethylcyclotetrasiloxane, phenyl trimethoxysilane, phenyl triethoxysilane, phenyl trichlorosilane, diphenyl dimethoxysilane, diphenyl diethoxysilane, diphenyl dichlorosilane, hexyl trimethoxysilane, octyl triethoxysilane, decyl trimethoxysilane, stearoxypropyl trimethoxysilane, vinyl trimethoxysilane, vinyl triethoxysilane, vinyltris-(β -methoxyethoxy)silane, vinyl trimethoxysilane, γ -methacryloxypropyl methyl dimethoxysilane, γ -methacryloxypropyl trimethoxysilane, γ -methacryloxypropyl methyl diethoxysilane, γ -isocyanate propyl triethoxysilane, 3-triethoxysilylpropylsuccinic anhydride, octadecyldimethyl-(3-trimethoxysilylpropyl)ammonium chloride, dimethylhexadecyl-(3-trimethoxysilylpropyl)ammonium chloride, methoxy(ethoxy)_n(propoxy)_mpropylmethyl dialkoxysilane, methoxy(ethoxy)_n(propoxy)_mpropyltrialkoxysilane, a compound (A) derived from γ -glycidoxypropyl triethoxysilane, γ -glycidoxypropyl methyl diethoxysilane and another substance, such as N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed protein and N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)

lyl)propoxy]propyl hydrolyzed protein, a compound (A) derived from a silane coupling agent such as β -(3,4-epoxycyclohexyl)ethyltrimethoxsilane, γ -[N-(β -aminoethyl)amino]propylmethyldimethoxsilane, γ -[N-(β -aminoethyl)amino]propyltrimethoxsilane, γ -aminopropyltrimethoxsilane, γ -aminopropyltriethoxsilane, γ -(N-phenylamino)propyltrimethoxsilane, vinyltrimethoxsilane, vinyltriethoxsilane, vinyltris-(β -methoxyethoxy)silanevinyltrichlosilane, γ -methacryloxypropylmethyldimethoxsilane, γ -methacryloxypropyltrimethoxsilane, γ -methacryloxypropylmethyldiethoxsilene, γ -methacryloxypropyltriethoxsilane, γ -chloropropyltrimethoxsilane, γ -mercaptopropyltrimethoxsilene, γ -isocyanate propyltriethoxsilane and 3-triethoxysilylpropyl-succinic anhydride.

[0107] The above-described series of surface treatments may be combined.

[0108] In the curing treatment of the instant invention, the strength of a wall of a microcapsule containing core material can be increased by further progressing the polycondensation reaction by removal of alcohol generated in hydrolysis of an alkoxy silane, which is a kind of the compound (A), or by dehydration due to the lapse of time or by heating and removal of water out of the reaction system, and the like. The temperature of the reaction solution is preferably 30°C or more. Heating at the boiling point of water in the reaction system is particularly preferable, although the boiling point may be changed by control of pressure. The above-described dehydration due to the lapse of time occurs since the siloxane condensation naturally progresses at neutral pH. The removal of water out of the system means for example distilling off (condensed water obtained by cooling of solvent vapor is removed out of the reaction system without returning it to the reaction system).

[0109] In thus obtained microcapsule containing core material, it is preferable that the weight of the core material is from about 0.01 to 99% by weight based on the weight of the microcapsule containing core material. This ratio of the weight of the core material to the weight of the microcapsule containing core material is hereinafter referred to "core weight ratio". According to the present invention, a wide range of the core weight ratio can be obtained, the thickness of the capsule wall is easily controlled by correlating the core weight ratio with the particle size.

[0110] The microcapsule containing core material has sufficient water resistance when it is used at a pH around neutral.

[0111] The strength of the capsule depends on the kind of the compound (A) used, particle size, curing conditions, and core weight ratio. As an example, in the case of a microcapsule produced for cosmetics having a particle size of 1 to 2 μ m and a core weight ratio of 90%, even if it was compounded in a cosmetic via mechanical mixing process and applied on skin, no decomposition was recognized.

[0112] The microcapsule containing core material produced according to the present invention can be treated by freeze-drying and spray-drying to be made into a powder.

[0113] The intake ratio of a core material into a microcapsule containing core material produced according to the present invention is from about 50 to 99.9% on a weight to weight basis, and in preferable cases, from about 80 to 98% on a weight to weight basis. This intake ratio shows how much % of a core material added is incorporated in the capsule.

[0114] Though the microcapsule produced according to the above-explained method exerts an excellent effect, incorporation of a core material into the capsule is not necessarily complete. A part of the core material may remain in the continuous phase, and may continuously leak out of the capsule into continuous phase with the lapse of time.

[0115] When a part of the core material remains in the continuous phase, and continuously leaks out of the capsule into the continuous phase with the lapse of time, various undesirable problems may occur.

[0116] For example, an object of preventing contact of the core material with skin, which is suggested in cosmetic fields and the like, can not be attained when the core material remains in the continuous phase or leaks into the continuous phase. Further, although it is suggested that an unstable material which is unstable and discolors with the lapse of time when exposed to outer atmosphere is incorporated into a microcapsule for insulation from the atmosphere and prevention of discoloring with the lapse of time, the object of the invention can not fully be accomplished if incorporation of the core material into the capsule is not complete.

[0117] In addition to the object mentioned above, there is another object of the present invention, which is to provide a microcapsule having a capsule wall made of a specific organopolysiloxane and a method for producing the same in which the amount of a core material that has not been incorporated into a capsule is minimum, and leaking of the core material out of the capsule in later use is minimum.

[0118] That is, the present invention provides a microcapsule containing core material wherein the capsule wall is made of organopolysiloxane synthesized by polycondensation of a compound (B), wherein at least one compound selected from the group consisting of hydrolyzable silanes and hydrolyzable polysiloxanes is added to the core material.

[0119] The present invention further provides a microcapsule containing core material wherein the capsule wall is made of organopolysiloxane synthesized by polycondensation of a compound (B), and the surface of the formed capsule wall is treated at least once with a hydrolysate of at least one compound selected from the group consisting of hydrolyzable silanes and hydrolyzable polysiloxanes.

[0120] The present invention further provides a method for producing a microcapsule containing core material, com-

prising a step wherein at least one compound selected from the group consisting of hydrolyzable silanes and hydrolyzable polysiloxanes is added to a core material, and a step wherein a compound (B) is polycondensed to synthesize organopolysiloxane to form a capsule wall.

[0121] The present invention further provides a method for producing a microcapsule containing core material, comprising a step wherein a compound (B) is polycondensed to synthesize organopolysiloxane to form a capsule wall, and a step wherein the surface of the formed capsule wall is treated at least once with a hydrolysate of at least one compound selected from the group consisting of hydrolyzable silanes and hydrolyzable polysiloxanes.

[0122] In the microcapsule containing core material of the present invention, at least one compound selected from the group consisting of hydrolyzable silanes and hydrolyzable polysiloxanes is added to a core material, or the surface 10 of the formed capsule wall is treated at least once with a hydrolysate of at least one compound selected from the group consisting of hydrolyzable silanes and hydrolyzable polysiloxanes, so that the amount of the core material which has not been incorporated into the capsule is minimum, or leaking out of the core material of the capsule in later use is minimum.

[0123] Herein, the term "hydrolyzable silanes" and "hydrolyzable polysiloxanes" respectively mean silanes and polysiloxanes which generate a silanol group by being hydrolyzed. As the hydrolyzable silanes and hydrolyzable polysiloxanes to be added to a core material or to be used for the treatment of the surface of the formed capsule wall, methyltrichlorosilane, methyl dichlorosilane, dimethyl dichlorosilane, trimethylchlorosilane, phenyltrichlorosilane, diphenyl dichlorosilane, methyl trimethoxysilane, methyl triethoxysilane, phenyl trimethoxysilane, phenyl triethoxysilane, diphenyl dimethoxysilane, diphenyl diethoxysilane, hexyl trimethoxysilane, octyl triethoxysilane, decyl trimethoxysilane, 20 tetramethoxysilane, tetraethoxysilane and $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_f[\text{MeZSiO}]_g\text{SiMe}_3$ (f represents an integer from 5 to 50, and g represents an integer from 2 to 100 and Z represents hydrogen or an alkoxy group) are exemplified. Particularly preferable examples thereof include tetramethoxysilane, tetraethoxysilane, methyltrichlorosilane, $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_f[\text{MeZSiO}]_g\text{SiMe}_3$ (f represents an integer from 5 to 50, and g represents an integer from 2 to 100, $f/g = 0.1$ to 20, weight-average molecular weight (M.W.) = 200 to 10000, and Z represents hydrogen, a methoxy group or ethoxy group) and the like.

[0124] At least one compound selected from hydrolyzable silanes and hydrolyzable polysiloxanes is usually added to a core material previously, and added to the continuous phase together with the core material.

[0125] The treatment of the surface of the formed capsule wall with a hydrolysate of at least one compound selected from the group consisting of hydrolyzable silanes and hydrolyzable polysiloxanes (hereinafter, referred to as over coat 30 treatment) is conducted at least once. It is conducted after mixing and emulsification, and usually before surface treatment of the capsule wall with a compound (A) and the like, namely, prevention of coagulation and curing treatment of the capsule wall. This over coat treatment is usually conducted by adding to the continuous phase at least one compound selected from hydrolyzable silanes and hydrolyzable polysiloxanes. The over coat treatment is preferably conducted with stirring at approximately the same temperature as that in the mixing and emulsification. The amount added 35 of at least one compound selected from the group consisting of hydrolyzable silanes and hydrolyzable polysiloxanes is from 0.1 to 30 mol, preferably from 0.5 to 10 mol per 100 of the total mol number of Si used for formation of the capsule wall.

[0126] If the intake ratio is not sufficiently high, purification such as removal of a core material which has not been incorporated in, and the like is usually required. Examples of the purification methods are as follows.

[0127] One purification method is that in which a liquid phase not dispersing the capsule and unmixable with the other liquid phase dispersing a capsule is added, said two liquid phases are mixed completely, then both liquids are separated by decantation or by liquid separation, after separation of the two phases, to transfer impurities to other liquid phase. When both liquid phases are not easily separated, centrifugal separation may be adopted. Further, when both liquid phases are not easily separated, liquid which is miscible with the liquid phase dispersing a capsule may be further 45 added to wash and separate the capsule.

[0128] Another purification method is that in which a microcapsule containing core material precipitated or floated by centrifugal separation is collected portion-wise. In this case, after the above-described procedure, impurities are removed together with a solvent. The collected microcapsule is re-dispersed into a solvent which can disperse the capsule. This procedure is repeated.

[0129] There is a method by ultrafiltration as another purification method. In this purification method by ultrafiltration, impurities eluted by ultrafiltration are removed, and the concentrated microcapsule is re-dispersed into a solvent which can disperse a microcapsule containing core material. This procedure is repeated.

[0130] The microcapsule containing core material of the present invention is bio-inactive, and the capsule wall thereof has thermal and mechanical stability and light resistance which are general basic properties of an organopolysiloxane.

[0130] The present invention is advantageous also in the point of cost since a microcapsule containing core material can be produced directly from a compound (A) such as an alkoxy silane, halogenated silane, hydrogensilane and polysiloxane. In addition, a wide range of microcapsules containing a core material can be easily designed according to various objects by combining various compounds (A).

[0131] The microcapsule containing core material of the present invention having such various properties can be widely applied to pharmaceuticals, liquid crystal, chemical products, recording materials, cosmetics, aromatics, enzymes, agriculture, adhesives, fiber, foods, catalysts, detergents, coloring matters, paints, preservatives and solvents.

5 [0132] For example, when a microcapsule containing core material of the present invention using a ultraviolet ray absorber as the core material is applied to cosmetics, the following merits are obtained as compared with the case in which a ultraviolet ray absorber itself is compounded in cosmetics.

1. Safety of cosmetics increases since permeation of a ultraviolet ray absorber into skin decreases.
- 10 2. A more stable formulation becomes possible in formulation systems in which stable formulations are conventionally difficult.
3. When a ultraviolet ray absorber itself is compounded in cosmetics, addition of a stabilizer may be required for preventing yellowing of the ultraviolet ray absorber. However, there is no necessity of a stabilizer in this invention.
- 15 4. When an ultraviolet ray absorber such as ethylhexylmethoxycinnamic acid is compounded itself, tackiness and the like occur, and when an ultraviolet ray absorber such as methoxybutylbenzoylmethane is compounded itself, a crystal is deposited to cause roughness. However, in this invention, these problems are solved, and the use feeling of the cosmetics is increased. Further, the adhesion of the cosmetics also increases.
- 20 5. When an ultraviolet ray absorber itself is compound in a formulation having high water content such as a lotion it is necessary to add a certain amount of a surfactant. However, according to the present invention, there is no need of addition of a surfactant or only a small amount of a surfactant should be added, therefore, a ultraviolet ray absorber can be easily compounded. Further, methoxybutylbenzoylmethane can not be easily compounded since it manifests poor solubility and the degree of solubility thereof decreases by the influence of other compounding components. In the present invention, however, compounding thereof is easy. Namely, according to the present invention, compatibility with other compounding components (raw material of cosmetics, oil and solvent) increases.
- 25 6. Ultraviolet ray absorbing effect (SPF value), namely effect for protecting humane body from a ultraviolet ray, increases.

[0133] When a microcapsule containing an ultraviolet ray absorber as the core material is applied to cosmetics, the particle size of the microcapsule is preferably from 0.05 µm to 50 µm, more preferably from 0.3 µm to 30 µm, and the compounding amount (by weight) of the ultraviolet ray absorber is preferably from 0.1% to 50%, more preferably from 0.5% to 30%, based on the amount of the microcapsule.

[0134] When the microcapsule containing core material of the present invention is used for e.g. pharmaceuticals, cosmetics, coloring matters, following ingredients, for example, are cooperatively used with the microcapsule: fatty acids particularly higher fatty acid, hydrocarbons, organic solvents, esters, phenols, silicones, silanes, metal alkoxides, alcohols particularly higher alcohol, animal and vegetable oils, extracted components, electrodonative coloration organic compounds, coloring matters, ultraviolet ray absorbers, vitamins, effective drug components, aroma components, preservative, sterilizer, salts; amino acid and its derivatives, protein, hydrolyzed protein and its derivatives, saccharides, polysaccharide, enzymes and fluorocarbon-like substances, which are exemplified as the core material in the above paragraphs; and surfactants classified into anionic, cationic, nonionic, and amphoteric surfactants which includes betaine type surfactant fatty acid salt, fatty acid hydrolyzed protein condensate, sulfate type surfactant, phosphate type surfactant, polyester and its derivatives.

Examples

45 [0135] Objects, characteristics and merits of the present invention are apparent from the following descriptions referring to various examples of the present invention, however, these descriptions are only illustrative and are not intended to restrict the scope of the present invention. All % and part in the following Examples are by weight unless otherwise stated.

50 Analysis method 1

[0136] About 10 g of the dispersion of a microcapsule containing core material is weighed correctly, the water content of the dispersion of the microcapsule containing core material is measured with an infrared moisture meter LIBROR EB-280MOC (trade name) manufactured by Shimadzu Corp. From this result, the weight of the non-water portion in the dispersion containing a microcapsule [microcapsule containing core material + free core material (core material which has not been incorporated into a capsule) + ash] is calculated. In the case of an oil-in-water type capsule, the weight of the dispersion containing a capsule is the weight of [water + microcapsule containing core material + free core material + ash]. When the water content is measured according to this Analysis method 1, the weight of the non-water portion in

the dispersion [microcapsule containing core material + free core material + ash] is calculated from the measured results.

Analysis method 2

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[0137] The concentration of Na in a capsule dispersion is measured by an ICP emission spectral analysis device SPS1700HVR (trade name) manufactured by Seiko Densi Kogyo Ltd., and the weight of NaCl in the dispersion containing a microcapsule is calculated. As described in the above-described Analysis 1, it is believed that the dispersion containing a microcapsule contains also ash, and almost all portions other than silica in the ash are occupied by NaCl. 10 Therefore, the amount of NaCl is measured by this Analysis method 2, and the result is used as an ash amount in calculating the core weight ratio, as described later.

Analysis 3

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[0138] About 1 g of dispersion of a microcapsule containing core material is weighed correctly, and then is transferred into a 500 ml separating funnel while being washed with about 100 ml of water. 100 ml of n-hexane is added and the mixture is sufficiently shaken, then, allowed to stand still. After separation of liquid phase, 100 ml of the n-hexane-washed solution is transferred to another vessel. This separation operation is repeated three times, the resulting n-hexane-extracted solutions are combined, and concentrated correctly to 100 ml. 1 μ l of this n-hexane extracted solution is drawn into a microsyringe, and subjected to liquid chromatography. The weight of free core material which has not been incorporated into the microcapsule, existing in about 1 g of the dispersion of the microcapsule containing core material, was measured based on a calibration curve of standard concentration separately made, and the weight of a free core material in the dispersion containing a microcapsule is calculated.

20

Analysis 4

[0139] About 0.1 g of the resulting dispersion of a microcapsule containing core material is weighed correctly, and to this is added 5 ml of a 5N sodium hydroxide aqueous solution and the mixture is stirred for one hour at 50°C and cooled to room temperature. This is transferred into a 500 ml separating funnel while being washed with about 100 ml of water.

30

100 ml of n-hexane is added and the mixture is sufficiently shaken, then, allowed to stand still. After separation of the liquid phase, 100 ml of the n-hexane-washed solution is transferred to another vessel. This separation operation is repeated three times, the resulting n-hexane-extracted solutions are combined, and concentrated correctly to 100 ml. 1 μ l of this n-hexane solution is drawn into a microsyringe, and subjected to liquid chromatography. The total weight of a free core material which has not been incorporated into the microcapsule and a core material which has been incorporated into the microcapsule existing in about 0.1 g of the resulting dispersion of the microcapsule containing core material, was determined based on a calibration curve of a standard concentration that was separately made.

[0140] Core weight ratio, in terms of % by weight of the amount of a core material incorporated into a microcapsule based on the weight of the microcapsule is obtained by the following formula:

40

$$\frac{[(\text{value by Analysis method 4}) - (\text{value by Analysis method 3})]}{[(\text{value by Analysis method 1}) - (\text{value by Analysis method 2}) - (\text{value by Analysis method 3})]} \times 100$$

Analysis method 5

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[0141] About 0.1 g of the resulting dispersion of a microcapsule containing core material is weighed, and about 5 ml of water is added to this. One drop of this is placed on a glass plate and covered by a cover glass, then, observed by an optical microscope at a magnification of 1000, and particle size distribution is visually measured.

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Analysis method 6

[0142] The particle size distribution of the resulting microcapsule containing core material is measured by SALD-2000 (trade name) manufactured by Shimadzu Corp.

55

Test method 1

[0143] One drop (about 50 μ l) of a dispersion of a microcapsule containing core material diluted by 20-fold is sandwiched between 2 pieces of glass plates that are 1 cm square and have a thickness of 2 mm, and this is placed on a

horizontal hard base plate and a pressure of 1.5 kg/cm² is applied from the upper side. After application of the pressure, it is observed if the microcapsule is broken or not.

Example 1

5 Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of methoxy (ethoxy) n-propyldihydroxymethylsilane, methyltriethoxysilane and phenyltriethoxysilane.

10 1) Preparation of prepolymer of capsule wall

[0144] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 90 g of water, 10 g of a polyoxyethylene-modified silicone (KF-354A (trade name) manufactured by Shin-Etsu 15 Silicone Co., Ltd., and produced by substituting both ends of methoxy (ethoxy) n-propyldihydroxymethylsilane with trimethyl silyl groups.) and 0.2 g of 18% hydrochloric acid. A mixture of 4.4 g of methyltriethoxysilane and 1.2 g of phenyltriethoxysilane was added dropwise from the dropping funnel at 50°C with stirring. The mixture was further stirred for 6 hours at 50°C, then, 1.6g of 4% aqueous sodium hydroxide solution was added dropwise with stirring to control the pH to 7.0. Thereafter, the mixture was stirred for 1 hour at 50°C.

20 2) Addition of core material and emulsification

[0145] 5.4 g of 2-ethylhexyl p-methoxycinnamate was added to the reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

25 3) Prevention of coagulation and curing treatment of capsule wall

[0146] 0.5 g of trimethylchlorosilane was added to the solution prepared in the process 2) in a reaction vessel with stirring at 600 rpm and 50°C then, immediately, 1 g of a 20% aqueous sodium hydroxide solution was added dropwise. 30 The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 6 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing a core material.

Comparative Example 1

35 Polymerization is conducted at an interface between a continuous phase and a core material in the production of microcapsule containing 2-ethylhexyl p-methoxycinnamate and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of methoxy (ethoxy) n-propyldihydroxymethylsilane, methyltriethoxysilane and phenyltriexhosilane.

40 1) Preparation of capsule wall

[0147] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 90 g of water, 10 g of a polyoxyethylene-modified silicone (KF-354A (trade name) manufactured by Shin-Etsu 45 Silicone Co., Ltd.) and 0.2 g of 18% hydrochloric acid. Thereto, a mixture of 4.4 g of methyltriethoxysilane and 1.2 g of phenyltriethoxysilane was added dropwise from the dropping funnel at 50°C with stirring. The mixture was further stirred for 6 hours at 50°C, then, 5.4 g of 2-ethylhexyl p-methoxycinnamate was added with stirring of the reaction solution at 600 rpm. Further, the mixture was stirred for 4 hours at 600 rpm, then, 1.9 g of a 4% aqueous sodium hydroxide 50 solution was added dropwise with stirring, to control the pH to 7.0. Thereafter, the mixture was stirred for 1 hour at 50°C.

2) Prevention of coagulation and curing treatment of capsule wall.

[0148] 3 g of trimethylchlorosilane was added to the solution prepared in the process 1) with stirring at 600 rpm and 50°C in the reaction vessel, then, 5.6 g of a 5N aqueous sodium hydroxide solution was added dropwise immediately. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 6 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a product. An adhesive substance adhered to the wall of the reac-

tion vessel, and only oil was separated in the about same amount with that of 2-ethylhexyl p-methoxycinnamate added.

Example 1A

- 5 Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and having a capsule wall made of organo-polysiloxane composed of a co-polycondensate of the hydrolysate of methoxy(ethoxy)n-propyldihydroxymethylsilane, methyltriethoxysilane and phenyltriethoxysilane.

[0149] A microcapsule containing core material was produced in the same manner as in Examples 1 except that 10 g of a polyoxyethylene-modified silicone was replaced with 3 g of polyethoxypropyltrimethoxysilane (KBM-641 manufactured by Shin-Etsu Silicone Co., Ltd.), the amounts of 4% aqueous sodium hydroxide solution, 2-ethylhexyl p-methoxycinnamate, trimethylchlorosilane and 20% aqueous sodium hydroxide solution were changed to 97g, 4.2g, 1.7g, 4.0g, 1.0g and 1.8g respectively, and the temperature at stirring after the pH was controlled to 7.0 was changed to 20°C.

[0150] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

20	Water dispersion of a capsule having a diameter from 0.3 to 10 µm, mainly from 1 to 2 µm Components excepting water	107 g 14. 0%
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[0151] In Example 1, a microcapsule containing core material was produced by using polyether-modified silicone, KF-354A (trade name), as a compound (A) carrying a hydrophilic group, hydrolysing this to prepare a prepolymer, adding a core material and conducting emulsification. However, when a polymer was produced at the interface between the core material and the continuous phase as in Comparative Example 1, a microcapsule containing core material was not formed, and the polymer was separated from the core material. In Example 1A, though a trialkoxysilane carrying a polyether group, KBK-641 (trade name), was used as a compound (A) carrying a hydrophilic group, a microcapsule containing core material could be produced like in Example 1.

[0152] The microcapsule containing core material that was obtained in Example 1A was tested to see if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 2

- 35 Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and having a capsule wall made of organo-polysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen, methyltriethoxysilane and phenyltriethoxysilane

1) Preparation of prepolymer of capsule wall

40 [0153] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 135 g of water, 15 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen (number-average molecular weight of the hydrolyzed collagen is about 2000) and 3.6 g of 18% hydrochloric acid. Thereto, a mixture of 45.9 g of methyltriethoxysilane and 12.4 g of phenyltriethoxysilane was added dropwise from the dropping funnel at 50°C with stirring.

[0154] The mixture was further stirred for 6 hours at 50°C. Then, 2.9 g of a 25% aqueous sodium hydroxide solution was added dropwise with stirring to control the pH to 7.0, and the mixture was further stirred for 1 hour at 50°C.

50 2) Addition of core material and emulsification

[0155] 389 g of 2-ethylhexyl p-methoxycinnamate was added to the reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

55 3) Micronization

[0156] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes to micronize the components.

4) Prevention of coagulation and curing treatment of capsule wall

- [0157] 3.0 g of trimethylchlorosilane was added to the solution prepared in the process 3) in the original reaction vessel with stirring at 600 rpm and 50°C, then, 4.4 g of a 25% aqueous sodium hydroxide solution was added dropwise immediately. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 2 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing core material.
- [0158] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 - 5 giving the following results.

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15	Water dispersion of a capsule having a diameter from 0.3 to 5 µm , mainly from 1 to 2 µm Components excepting water	850 g 50%
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The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 4%.

The amount of 2-ethylhexyl p-methoxycinnamate contained in the capsule was 84%.

- [0159] Then, the free 2-ethylhexyl p-methoxycinnamate in the dispersion was removed by washing with hexane, and a microcapsule containing 2-ethylhexyl p-methoxycinnamate was obtained in purified condition. When the addition of methyltrichlorosilane and the following series of neutralization treatments were deleted in the prevention of coagulation and curing treatment of a capsule wall in the process 4), no difference from the present examples was recognized with the naked eyes, however, microscope observation revealed mutual adhesion of the microcapsule and partial coagulation. In the present examples, such coagulation was not recognized.
- [0160] The microcapsule containing core material obtained in Example 2 was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 2A

- 30 Production of a microcapsule containing a mixture of 2-ethylhexyl p-methoxycinnamate and 4-t-butyl-4' - methoxydibenzoylmethane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen, methyltriethoxsilane and phenyltriethoxsilane
- 35 [0161] A microcapsule containing core material was produced in the same manner as in Example 2 except that 389g of 2-ethylhexyl p-methoxycinnamate was replaced with a mixture obtained previously by dissolving 19.5g of 4-t-butyl-4' - methoxydibenzoylmethane in 78.2g of 2-ethylhexyl p-methoxycinnamate and the dropwise addition of 2.9g of a 25% aqueous sodium hydroxide solution and the following stirring were conducted at 20°C.
- [0162] The dispersion of the resulting microcapsule confining core material was analyzed according to Analysis methods 1 and 5 giving the following results.

45	Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm Components excepting water	315 g 42.3%
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- [0163] As described above, in this Example 2A, 4-t-butyl-4'-methoxydibenzoylmethane as second core material could be simultaneously incorporated in a microcapsule in addition to 2-ethylhexyl p-methoxycinnamate.
- 50 [0164] The microcapsule containing core material obtained in Example 2A was tested if the capsule thereof was broken in the above-described Test method 1 or not. NO breakage of the capsule was found.

55

Example 2B

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed wheat protein, methyltriethoxysilane and phenyltriethoxysilane

1) Preparation of prepolymer of capsule wall

[0165] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 283 g of water, 16.8 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed wheat protein (number-average molecular weight of the hydrolyzed wheat protein is about 400) and 4.5 g of a 20% aqueous sodium hydroxide solution. Thereto, a mixture of 24 g of methyltriethoxysilane and 3.2 g of phenyltriethoxysilane was added dropwise from the dropping funnel at 50°C with stirring.

[0166] The mixture was further stirred for 6 hours at 50°C. Then, 4.1 g of a 18% hydrochloric acid was added dropwise with stirring to control the pH to 7.0, and the mixture was further stirred for 1 hour at 50°C.

2) Addition of core material and emulsification

[0167] 12.3 g of 2-ethylhexyl p-methoxycinnamate was added to the reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

3) Micronization

[0168] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes to micronize the components.

4) Prevention of coagulation and curing treatment of capsule wall

[0169] 1.2 g of trimethylchlorosilane was added to the solution prepared in the process 3) in the original reaction vessel with stirring at 600 rpm and 50°C, then, 1.4 g of a 20% aqueous sodium hydroxide solution was added dropwise immediately to control the pH at 5.5. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 2 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing core material.

[0170] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

40

Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm	595 g
Components excepting water	11%

[0171] As described above, in this Example 2B, a microcapsule containing core material was produced using a compound (A) carrying a hydrophilic group composed of hydrolyzed wheat protein. The hydrolysis of the compound (A) was conducted under basic conditions.

Comparative Example 2

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[0172] The same procedure and ingredients used in Example 2B were utilized except that the hydrolysis of the silane was conducted at an acidic pH instead of hydrolysis at basic pH as occurred in Example 2B. A large amount of adhesive materials adhered to the inner wall of the reaction vessel, and production of a microcapsule could not continue.

55

Example 2C

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed soybean protein, methyltriethoxsilane and phenyltriethoxsilane

1) Preparation of prepolymer of capsule wall

[0173] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 177 g of water, 9.3 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed soybean protein (number-average molecular weight of the hydrolyzed soybean protein is about 350) and 3.5 g of a 20% aqueous sodium hydroxide solution. Thereto, a mixture of 10 g of methyltriethoxsilane and 2.7 g of phenyltriethoxsilane was added dropwise from the dropping funnel at 50°C with stirring.

[0174] The mixture was further stirred for 6 hours at 50°C. Then, 3.2 g of a 18% hydrochloric acid was added dropwise with stirring to control the pH to 7.0, and the mixture was further stirred for 1 hour at 50°C.

2) Addition of core material and emulsification

[0175] 6.5 g of 2-ethylhexyl p-methoxycinnamate was added to the reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

3) Micronization

[0176] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes to micronize the components.

4) Prevention of coagulation and curing treatment of capsule wall

[0177] 2.4 g of trimethylchlorosilane was added to the solution prepared in the process 3) in the original reaction vessel with stirring at 600 rpm and 50°C, then, 1.2 g of a 20% aqueous sodium hydroxide solution was added dropwise to control the pH to 5.5. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 6 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing core material.

[0178] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

40	Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm Components excepting water	360 g 7.6%
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[0179] As described above, in this Example 2C, a microcapsule containing core material was produced using a compound (A) carrying a hydrophilic group composed of hydrolyzed soybean protein. The hydrolysis of the compound (A) was conducted under basic conditions.

[0180] The microcapsule containing core material obtained in Example 2C was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

50 Example 2D

[0181] A microcapsule containing core material was produced in the same manner as in Examples 2 except that 8.7 g of hexyltrimethoxsilane (KBM-3063 manufactured by Shin-Etsu Silicone Co., Ltd.) was used instead of the phenyltriethoxsilane, the amounts of methyltriethoxsilane and 2-ethylhexyl p-methoxycinnamate were changed to 38.3 g and 87.4 g respectively, and treatment with methyltrichlorosilane was not conducted.

[0182] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

5	Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm Components excepting water	507 g 23.6%
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[0183] The microcapsule containing core material obtained in Example 2D was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

10 Example 2E

[0184] A microcapsule containing core material was produced in the same manner as in Examples 2 except that 6.7 g of decyltrimethoxsilane (KBM-3103C manufactured by Shin-Etsu Silicone Co., Ltd.) was used instead of the phenyl-triethoxsilane, the amounts of methyltriethoxsilane and 2-ethylhexyl p-methoxycinnamate were changed to 30.0 g and 6.1 g respectively, and treatment with methyltrichlorosilane was not conducted.

[0185] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

20

25	Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm Components excepting water	300 g 11.9%
----	---	----------------

[0186] In these Example 2D and 2E, a microcapsule containing core material was produced even if a hydroxysilane having a hydrophobic group different to that used in Example 2 was used.

[0187] The microcapsule containing core material obtained in Example 2E was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

30 Example 2F

[0188] A microcapsule containing core material was produced in the same manner as in Examples 2 except that 15g of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen having a number average molecular weight at peptide portion of about 2000 was used instead of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen.

[0189] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

40

45	Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm Components excepting water	687 g 54.3%
----	---	----------------

[0190] As described above, in this Example 2F, a microcapsule containing a core material was produced even if N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen was used instead of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen.

[0191] The microcapsule containing core material obtained in Example 2A was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 2G

[0192] A microcapsule containing core material was produced in the same manner as in Examples 2 except that 15g of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen was used instead of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen, 22.8g of stearylxypropyltrimethoxsilane(KBM-6000 manufactured by Shin-Etsu Silicone Co., Ltd.) was used instead of phenyltriethoxsilane and the amount of 2-ethylhexyl p-methoxy-cinnamate was changed to 60 g.

[0193] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 - 5 giving the following results.

5

Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm	400 g
Components excepting water	25%

10 The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 6%.

The amount of 2-ethylhexyl p-methoxycinnamate contained in the capsule was 40%.

[0194] As described above, in this Example 2G, a microcapsule containing a core material was produced even if a hydroxysilane having a hydrophobic group different to that of the above mentioned Example 2F.

[0195] The microcapsule containing core material obtained in Example 2G was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 2H

[0196] A microcapsule containing core material was produced in the same manner as in Examples 2 except that 20 45.9g of methyltriethoxsilane was replaced with 19.1g of dimethyldiethoxsilane and 23.0g of methyltriethoxsilane and the amount of 2-ethylhexyl p-methoxycinnamate was changed to 97.7 g.

[0197] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

25

Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm	460 g
Components excepting water	27.1%

30

[0198] As described above, in this Example 2H, a microcapsule containing a core material was obtained even if a part of trihydroxysilane was replaced with a dihydroxysilane.

[0199] The microcapsule containing core material obtained in Example 2H was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

35

Example 2I

[0200] A microcapsule containing core material was produced in the same manner as in Examples 2H except that 40 9.6g of octamethylcyclotetrasiloxane was used instead of dimethyldiethoxsilane.

[0201] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

45

Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm	425 g
Components excepting water	25.1%

50

[0202] As described above, in this Example 2I, a microcapsule containing a core material was obtained even if alkoxysilane used in Example 2H was replaced with a cyclosiloxane.

[0203] The microcapsule containing core material obtained in Example 2I was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 2J

55

[0204] A microcapsule containing core material was produced in the same manner as in Examples 2F except that 16.2g of isopropyl stearate and 4.1g of abietic acid was used instead of 2-ethylhexyl p-methoxycinnamate and homomixer treatment was not conducted.

[0205] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results

5

Water dispersion of a capsule having a diameter from 0.3 to 100 µm, mainly from 10 to 50 µm	226 g
Components excepting water	30%

- 10 [0206] As described above, in this Example 2J, a microcapsule containing abietic acid which is a solid resin at a room temperature was obtained by dissolving the abietic acid in isopropyl stearate
 [0207] The microcapsule containing core material obtained in Example 2J was tested if the capsule thereof was broken according to the above-described Test method 1 or not, to find that a capsule having a particle size of about 8 µm or more was broken. Particularly, in the condition wherein capsules having a particle size from 8 to 15 µm were broken, leaking of the core material out of the capsule was observed, and it was observed that the capsule wall and the core material are rounded respectively to form the shape of an "eight". However very little breakage was observed of a capsule having a particle size of less than 8 µm.
- 15

Example 2K

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- [0208] A microcapsule containing core material was produced in the same manner as in Examples 2F except that 15g of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed silk protein (fibroin) having a number average molecular weight at peptide portion of about 1000 was used instead of N-[2-hydroxy-3(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen.
 25 [0209] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

30

Water dispersion of a capsule having a diameter from 1 to 100 µm, mainly from 10 to 50 µm	375 g
Components excepting water	20 %

- 35 [0210] As described above, in this Example 2K, a microcapsule containing core material was obtained even if the compound (A) having hydrolyzed silk protein (fibroin), as a hydrophilic group, was used.
 [0211] The microcapsule containing core material obtained in Example 2K was tested if the capsule thereof was broken according to the above-described Test method 1 or not, to find that a capsule having a particle size of about 8 µm or more was broken. Particularly, in the condition wherein capsules having a particle size from 8 to 15 µm were broken, leaking of the core material out of the capsule was observed, and it was observed that the capsule wall and the core material are rounded respectively to form the shape of an "eight". However very little breakage was observed of a capsule having a particle size of less than 8 µm.
- 40

Example 2L

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- [0212] A microcapsule containing core material was produced in the same manner as in Examples 2F except that 10.5g of castor oil was used instead of 2-ethylhexyl p-methoxycinnamate, and the amounts of methyltriethoxsilane and phenyltriethoxsilane were changed to 38.2g and 10.3g, respectively.
 [0213] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

50

Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm	300 g
Components excepting water	15%

- [0214] As described above, in this Example 2L, a microcapsule containing castor oil which is a viscous liquid at a room temperature was obtained.

[0215] The microcapsule containing core material obtained in Example 2L was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 2M

[0216] A microcapsule containing core material was produced in the same manner as in Examples 2 except that the amounts of methyltriethoxysilane and phenyltriethoxysilane were changed to 17.0g and 4.6g, respectively, 0.5g of octadecyldimethyl-(3-trimethoxysilylpropyl)ammonium chloride was added simultaneously in adding them and 16.7g of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen having a number average molecular weight at peptide portion of about 2000 was used instead of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen.

[0217] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

15

Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm	370 g
Components excepting water	11.9 %

20

[0218] As described above, in this Example 2M, a microcapsule containing core material was obtained even if a compound having a cationic group was used as a part of monomer components for organopolysiloxane forming the capsule wall.

[0219] The microcapsule containing core material obtained in Example 2M was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 2N

[0220] A microcapsule containing core material was produced in the same manner as in Examples 2 except that 4.6g of retinol palmitate and 4.6g of isopropyl isostearate were used instead of 2-ethylhexyl p-methoxycinnamate.

[0221] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 - 5 giving the following results.

35

Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm	310 g
Components excepting water	14.8 %

40

The amount of free retinol palmitate in the dispersion was 0.1%.

The amount of retinol palmitate contained in the capsule was 9.9%.

[0222] As described above, in this Example 2N, a microcapsule containing retinol palmitate which is viscous at a room temperature was obtained by dissolving retinol palmitate in isopropyl isostearate.

[0223] The microcapsule containing core material obtained in Example 2M was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 2 O

[0224] A microcapsule containing core material was produced in the same manner as in Examples 2 except that 4.6g of tocopherol acetate and 4.6g of isopropyl isostearate were used instead of 2-ethylhexyl p-methoxycinnamate.

[0225] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

55

Water dispersion of a capsule having a diameter from 0.3 to 10 µm, mainly from 2 to 7 µm	324 g
Components excepting water	14.3 %

[0226] As described above, in this Example 2 O, a microcapsule containing tocopherol acetate which is a derivative of vitamin E was obtained by dissolving retinol palmitate in isopropyl isostearate.

5 [0227] The microcapsule containing core material obtained in Example 2 O was tested if the capsule thereof was broken according to the above-described Test method 1 or not, to find that a capsule having a particle size of about 8 μm or more was broken. Particularly, in the condition wherein capsules having a particle size from 8 to 10 μm were broken, leaking of the core material out of the capsule was observed, and it was observed that the capsule wall and the core material are rounded respectively to form the shape of an "eight". However very little breakage was observed of a capsule having a particle size of less than 8 μm .

10 Example 3

[0228] A microcapsule containing core material was produced in the same manner as in Examples 2 except that before treatment of trimethylchlorosilane in Examples 2, 3.0g of 18% hydrochloric acid was previously added to the reaction solution, and 10.6 g of octadecyldimethyl-(3-trimethoxysilylpropyl)ammonium chloride was added and 2.4 g of a 25% aqueous sodium hydroxide solution was added for neutralization.

15 [0229] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

20

Water dispersion of a capsule having a diameter from 0.3 to 5 μm , mainly from 1 to 2 μm	820 g
Components excepting water	61.1 %

25 [0230] According to the production process of a microcapsule containing core material in Example 3 except that the addition of octadecyldimethyl-(3-trimethoxysilylpropyl)ammonium chloride and the following series of neutralization treatments and the addition of methyltrichlorosilane and the following series of neutralization treatments were deleted, no difference from the present examples was recognized with the naked eyes, however, microscope observation revealed mutual adhesion of the microcapsule and partial coagulation. However, in the present examples 3, such coagulation was not recognized.

30 [0231] The microcapsule containing core material obtained in Example 3 was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 4

35

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen, methyltriethoxysilane and phenyltriethoxysilane

40 1) Preparation of prepolymer of capsule wall

[0232] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 405 g of water, 45 g of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen (number-average molecular weight of the hydrolyzed collagen is about 2000) and 10.8g of 18% hydrochloric acid. Thereto, a mixture of 137.7 g of methyltriethoxysilane and 37.1 g of phenyltriethoxysilane was added dropwise from the dropping funnel at 50°C with stirring.

45 [0233] The mixture was further stirred for 6 hours at 50°C. Then, 8.7 g of a 25% aqueous sodium hydroxide solution was added dropwise with stirring to control the pH to 7.0, and the mixture was further stirred for 1 hour at 50°C.

50 2) Addition of core material and emulsification

[0234] 126.9g of 2-ethylhexyl p-methoxycinnamate was added to the reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

55

3) Micronization

[0235] About a half of the reaction solution prepared in the process 2) was transferred to a vessel of a homomixer,

and treated by the homomixer at 50°C and 6000 rpm for 90 minutes to micronize the components. Further, this treated solution was treated by a microfluidizer [M110-E/H (trade name) manufactured by Microfluidex • International • Corporation] at 50°C and 1500 kg/cm² five times, to micronize the components.

5 4) Prevention of coagulation and curing treatment of capsule wall

[0236] 1.0 g of trimethylchlorosilane was added to the solution prepared in the process 3) in the original reaction vessel with stirring at 600 rpm and 50°C, then, 1.48 g of a 25% aqueous sodium hydroxide solution was added dropwise immediately. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 6 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing core material.

[0237] The dispersion of the microcapsule containing core material obtained in Example 4 was analysed according to the above-described Analysis methods 1 and Analysis method 6, to obtain the following results. In Example 4, since micronization was conducted using the microfluidizer as described above, the resulting microcapsule containing core material was in the range of nanocapsules. Therefore, regarding the microcapsule containing core material obtained in Example 4, the particle size distribution could not be measured by visual observation using the optical microscope according to Analysis method 5, and accordingly, measurement of particle size distribution by SALD-2000 (trade name) in Analysis method 6 was conducted.

20

Water dispersion of a capsule having a diameter from 0.3 to 1 µm, mainly from 0.4 to 0.7 µm	250 g
Components excepting water	20%

25

[0238] The microcapsule containing core material obtained in Example 4 was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 4A

30

[0239] A microcapsule containing core material was produced in the same manner as in Examples 4 except that, in "3) Micronization", remaining half of the reaction solution prepared in the process 2) in Example 4 was used, and the micronization treatment by a microfluidizer was not conducted.

[0240] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 6 giving the following results.

40

Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm	250 g
Components excepting water	20%

[0241] The microcapsule containing core material obtained in Example 4A was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

45

Example 5

1) Preparation of prepolymer of capsule wall

50 [0242] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 210 g of water, 90 g of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen (number-average molecular weight of the hydrolyzed collagen is about 2000) and 21.8g of 18% hydrochloric acid. Thereto, a mixture of 45.9 g of methyltriethoxysilane and 10.5 g of hexyltriethoxysilane was added dropwise from the dropping funnel at 50°C with stirring.

55 [0243] The mixture was further stirred for 6 hours at 50°C. Then, 22 g of a 25% aqueous sodium hydroxide solution was added dropwise with stirring to control the pH to 7.0, and the mixture was further stirred for 1 hour at 50°C.

2) Addition of core material and emulsification

[0244] 389g of 2-ethylhexyl p-methoxycinnamate was added to the reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

5 3) Micronization

[0245] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes to micronize the components.

10 4) Curing treatment of capsule wall

[0246] The solution prepared in the process 3) in the original reaction vessel was further heated to reflux with stirring at 150 rpm for 2 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a micro-15 capsule containing core material.

[0247] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis method 5 giving the following results.

Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm

20 5) Spray-drying

[0248] A part of the product obtained in the process 4) was spray-dried to give a powder. 0.1 g of this powder was added to 10 ml of water, and the mixture was dispersed by complete stirring, and observed according to Analysis method 5 to find the same observation results as those before the spray-drying.

25 Example 5A

Freeze-drying treatment of microcapsule containing core material

30 [0249] A part of the product obtained in the process 4) of Example 5 was freeze-dried without spray-drying treatment to give a powder. 0.1 g of this powder was added to 10 ml of water, and the mixture was dispersed by complete stirring, and observed according to Analysis method 5 to find the same observation results as those before the spray-drying.

Example 6

35 Purification using centrifugal separator of microcapsule containing core material

[0250] A microcapsule containing core material was produced in the same manner as in Example 2 except that 8.7 g of hexyltrimethoxysilane was used instead of phenyltriethoxysilane in Example 2, 15 g of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen (number-average molecular weight of hydrolyzed collagen is about 2000) was used instead of N-[2-hydroxy-3-(3'-triethoxysilyl)propoxy]propyl hydrolyzed collagen, 38.3 g of methyltriethoxysilane was used, 35.3 g of 2-ethylhexyl p-methoxycinnamate was used, and treatment with methyltrichlorosilane was not conducted.

[0251] The resulting microcapsule containing core material was centrifuged (4000 rpm, 10 minutes), the supernatant was removed, then, 2 to 5 volumes of water was added to the precipitant and suspended again, then, again centrifuged (4000 rpm, 10 minutes). This operation was repeated three times to obtain a microcapsule containing core material having controlled concentration.

[0252] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

50

55	Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm Components excepting water NaCl content in the dispersion before centrifugal separation treatment NaCl content in the dispersion after centrifugal separation treatment	150 g 44 % 0.34% 0.02%
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[0253] As described above, it was recognized that NaCl reduces by centrifugal separation treatment.

Example 6A

5 Purification by ultrafiltration of microcapsule containing core material obtained in Example 2F

[0254] A part of the microcapsule containing core material obtained in Example 2F was ultrafiltrated, then, 2 to 5 volumes of water was added to the remaining material and dispersed again, then, again ultrafiltrated. This operation was repeated three times to obtain a microcapsule containing core material having controlled concentration.

10 [0255] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

15	Water dispersion of a capsule having a diameter from 1 to 10 µm, mainly from 3 to 7 µm	200 g
	Components excepting water	20 %
20	NaCl content in the dispersion before ultrafiltration treatment	0.38%
	NaCl content in the dispersion after ultrafiltration treatment	0.03%

[0256] As described above, it was recognized that NaCl reduces by ultrafiltration treatment.

Example 7

25 Production of a W/O type microcapsule having a capsule wall made of organopolysiloxane composed of a co-poly-condensate of the hydrolysate of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen, dimethyl-diethoxysilane and hexyltrimethoxysilane

30 1) Preparation of prepolymer of capsule wall

[0257] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 131 g of water, 9 g of N-[2-hydroxy-3-(3' - dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen (number-average molecular weight of the hydrolyzed collagen is about 400) and 8 g of 18% hydrochloric acid. Thereto, a mixture of 20.6 g of dimethyl-diethoxysilane and 57.3 g of hexyltriethoxysilane was added dropwise from the dropping funnel at 50°C with stirring.

[0258] The mixture was further stirred for 6 hours at 50°C. Then, 6.3 g of a 25% aqueous sodium hydroxide solution was added dropwise with stirring to control the pH to 7.0, and the mixture was further stirred for 1 hour at 50°C.

40 2) Addition of an oil phase and phase inversion and emulsification

[0259] 150g of Toluene was added to the reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

45 3) Micronization

[0260] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes to micronize the components.

50 4) Prevention of coagulation and curing treatment of capsule wall

[0261] 3.0 g of trimethylchlorosilane was added to the solution prepared in the process 3) in the original reaction vessel with stirring at 600 rpm and 50°C, then, 4.4 g of a 25% aqueous sodium hydroxide solution was added dropwise immediately. The temperature of the reaction solution was raised gradually to reflux and 85% of water was distilled off. The remaining mixture was further heated to reflux with stirring at 150 rpm for 6 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing core material.

[0262] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis

method 5 giving the following results.

5	Toluene dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 2 µm	241 g
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[0263] The dispersion was applied on a glass plate, and a film formed by evaporation of toluene was scratched to observe water drops on the surface of the glass plate. Further, this dispersion was mixed with water, then, allowed to stand still to find separation into two layers. The capsule dispersed in the toluene layer. From this observation, it was recognized that a microcapsule containing water and having hydrophobic surface could be produced.

Example 7A

[0264] A microcapsule containing core material was produced in the same manner as in Example 7 except that the amount of hexyltrimethoxysilane in Example 7 was changed from 573.3 g to 86.0 g; dimethyldiethoxysilane was not used; in the addition of an oil phase and phase inversion and emulsification of the process 2), 160 g of isopropyl isostearate was used instead of toluene used; in the prevention of coagulation and curing treatment of a capsule wall of the process 4), a equimolar of potassium hydroxide was used instead of sodium hydroxide; and 30.8 g of a 35% aqueous potassium chloride solution was added simultaneously in mixing isopropyl isostearate. [0265] The dispersion of the microcapsule containing core material obtained in Example 7A was analyzed according to the above-described Analysis method 5 to find the following result.

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A dispersion of a capsule having diameter of 0.3 to 5 µm, mainly of 1 to 2 µm in isopropyl isostearate	280 g
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[0266] When the dispersion in Example 7A was mixed with water and allowed to stand still, the mixture was separated into two layers, and the microcapsule containing core material was dispersed in the isopropyl isostearate layer. Thus, a W/O type microcapsule containing core material could be produced without using dialkoxysilane in this Example 7A unlike Example 7.

[0267] The microcapsule containing core material obtained in Example 7A was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 7B

[0268] A microcapsule containing core material was produced in the same manner as in Example 7 except that 71.6 g of hexyltrimethoxysilane and 16.7 g of phenyltriethoxysilane were used instead of dimethyldiethoxysilane and hexyltrimethoxysilane in Example 7, 34.4 g of a 36% L-ascorbic acid aqueous solution was added simultaneously in adding toluene, and 50% of water was distilled off before the treatment by the homomixer. [0268] The dispersion of the microcapsule containing core material obtained in Example 7B was analyzed according to the above-described Analysis method 5 to find the following result.

50	Toluene dispersion of a capsule having a diameter of 0.3 to 5 µm, mainly of 1 to 2 µm	216 g
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[0269] The dispersion in Example 7B was applied on a glass plate, and a film formed by evaporation of toluene was scratched to observe water drops on the surface of the glass plate. This dispersion was mixed with water, then, allowed to stand still to find separation into two layers and the microcapsule dispersed in the toluene layer. [0270] The microcapsule containing core material obtained in Example 7B was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of tie capsule was found.

Example 7C

- [0271] A microcapsule containing core material was produced in the same manner as in Example 7 except that 235 g of diisobutyladipate was used instead of toluene in Example 7, 106 g of a 10% aqueous solution of 2-phosphoric acid-L-ascorbylmagnesium was added simultaneously in adding thin diisobutyladipate, the product was purified by centrifugal separation and treated by the homomixer according to Example 6, then, almost all of water was distilled at 40°C under reduced pressure, then, the remaining water was distilled off by heating at atmospheric pressure.
- [0272] The dispersion of the microcapsule containing core material obtained in Example 7C was analyzed according to the above-described Analysis method 5 to find the following result.

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Toluene dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly of 1 to 2 µm	324 g
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- [0273] 200 ml of n-hexane was added to 20 g of the dispersion obtained in Example 7C, extracted with 100 ml of water and measured by a ultraviolet ray + visible light spectral photometer UV-1600 (trade name) manufactured by Shimadzu Corp., to find that 10% of the 2-phosphoric acids-L-ascorbylmagnesium added was liberated. Further, when 50 ml of chloroform was added to 2 g of the dispersion obtained in Example 7C and the mixture was stirred for 1 hour at 50°C, the capsule was broken. This was extracted with 100 ml of water and measured by a ultraviolet ray spectral photometer to find that 95% of the 2-phosphoric acid-L-ascorbylmagnesium added was recovered. As a result, it was known that the intaking ratio was 85%. Further, it has become apparent that free 2-phosphoric acid-L-ascorbylmagnesium can be removed by extraction with water and washing.
- [0274] When the dispersion in Example 7C was mixed with water and then allowed to stand still, the mixture was separated into two layers, and the microcapsule containing core material was dispersed into the diisobutyladipate layer.
- [0275] The microcapsule containing core material obtained in Example 7C was tested if the capsule thereof was broken in the above-described Test method 1 or not. No breakage of the capsule was found.

Example 8

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Production of microcapsule containing core material of liquid perfluoroether having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen, tetraethoxsilane and C₈F₁₇CH₂CH₂Si(OCH₃)₃ (KBM-7803 manufactured by Shin-Etsu Silicone Co., Ltd.)

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1) Preparation of prepolymer of capsule wall

- [0276] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 90g of water, 10g of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen (number-average molecular weight of the hydrolyzed collagen is about 2000) and 2.4g of 18% hydrochloric acid. Thereto, a mixture of 19.0g of tetraethoxsilane and 3.2g of C₈F₁₇CH₂CH₂Si(OCH₃)₃ (KBM-7803 manufactured by Shin-Etsu Silicone Co., Ltd.) was added dropwise from the dropping funnel at 50°C with stirring.

- [0277] The mixture was further stirred for 12 hours at 50°C. Then, 100g of a 0.6% aqueous sodium hydroxide solution was added dropwise with stirring to control the pH to 7.0, and the mixture was further stirred for 1 hour at 50°C.

2) Addition of liquid perfluoroether and emulsification

- [0278] A mixture of 6.8g of perfluoroether, Fomblin HC/R (manufactured by Motefious Co., Ltd., average molecular weight of 6250, CF₃[(OCF(CF₃)CF₂)n(OCF₂)m]OCF₃, n/m=20-40) and 3.2g of C₈F₁₇CH₂CH₂Si(OCH₃)₃ (KBM-7803 manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the reaction solution prepared in the process 1) with stirring at 500 rpm, and the mixture was further stirred for 4 hours at 500 rpm.

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- [0279] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes to micronize the components.

4) Prevention of coagulation and curing treatment of capsule wall

- [0280] 1.23 g of trimethylchlorosilane was added to the solution prepared in the process 3) in the original reaction vessel with stirring at 500 rpm and 50°C, then, 1.2 g of a 25% aqueous sodium hydroxide solution was added dropwise immediately. The temperature of the reaction solution was raised gradually to reflux with stirring at 500 rpm and 50°C. The mixture was further heated to reflux with stirring at 150 rpm for 6 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing core material as a milky white dispersion.
- [0281] The dispersion of the microcapsule containing core material obtained in Example 8 was analysed according to the above-described Analysis method 1 and Analysis method 5, to obtain the following results.

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Water dispersion of a capsule having a diameter from 5 to 10 µm	110 g
Components excepting water	17.1 %

- [0282] This dispersion could be freeze-dried.
- [0283] The microcapsule containing core material obtained in Example 8 was tested if the capsule thereof was broken according to the above-described Test method 1 or not, to find that a capsule having a particle size of about 8 µm or more was broken. Particularly, in the condition wherein capsules having a particle size from 8 to 10 µm were broken, leaking of the core material out of the capsule was observed, and it was observed that the capsule wall and the core material are rounded respectively to form the shape of an "eight". However very little breakage was observed of a capsule having a particle size of less than 8 µm.

25 Comparative Example 3

- 1) Preparation of prepolymer of capsule wall
- [0284] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 90g of water, 10g of N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed collagen (number-average molecular weight of the hydrolyzed collagen is about 2000) and 2.4g of 18% hydrochloric acid. Thereto, a mixture of 19.0g of tetraethoxysilane and 9.5g of C₈F₁₇CH₂CH₂Si(OCH₃)₃ (KBM-7803 manufactured by Shin-Etsu Silicone Co., Ltd.) was added dropwise from the dropping funnel at 50°C with stirring.
- [0285] The mixture was further stirred for 12 hours at 50°C. Then, 100g of a 0.6% aqueous sodium hydroxide solution was added dropwise with stirring to control the pH to 7.0, and the mixture was further stirred for 1 hour at 50°C.

- 2) Addition of liquid perfluoroether and emulsification
- [0286] 6.8g of perfluoroether, Fomblin HC/R (manufactured by Moteflous Co., Ltd., average molecular weight of 6250,-CF₃[OCF(CF₃)CF₂)n(OCF₂)m]OCF₃, n/m=20-40) was added to the reaction solution prepared in the process 1) with stirring at 500 rpm, and the mixture was further stirred for 4 hours at 500 rpm.

- 3) Micronization
- [0287] The reaction-solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes to micronize the components.

- 4) Prevention of coagulation and curing treatment of capsule wall
- [0288] 1.23 g of trimethylchlorosilane was added to the solution prepared in the process 3) in the original reaction vessel with stirring at 500 rpm and 50°C, then, 1.2 g of a 25% aqueous sodium hydroxide solution was added dropwise immediately. The temperature of the reaction solution was raised gradually to reflux with stirring at 500 rpm and 50°C. The mixture was further heated to reflux with stirring at 150 rpm for 6 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature. This reaction solution split into three phases.
- [0289] The dispersion of the microcapsule containing core material obtained in this Comparative Example was analysed according to the above-described Analysis method 5, to obtain the following results.
- [0290] No capsule was observed with the optical microscope. 260g of liquid separated into three phases was

obtained.

[0291] The microcapsule containing core material was not obtained in this Comparative Example. However, in Example 8, in which a part of the compound having a perfluoroalkane group, $C_8F_{17}CH_2CH_2Si(OCH_3)_3$ (KBM-7803 manufactured by Shin-Etsu Silicone Co., Ltd.), was added simultaneously in adding the core material, a microcapsule containing a liquid perfluoroether was obtained.

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Example 9

Production of microcapsule containing core material of 2-ethylhexyl p-methoxycinnamate having a capsule wall made
10 of organopolysiloxane composed of the hydrolysate co-polycondensate of methyltriethoxysilane and phenyltriethoxysi-
lane in gelatin aqueous solution

1) Preparation of prepolymer

15 [0292] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was charged with 120 g of water, and to this was added 6 g of gelatin as a thickening agent and mixture was heated to dissolve gelatin. The solution was cooled to 20°C, and the viscosity thereof was controlled to 50 mPa · s. 5.5 g of 10% hydrochloric acid was added to this solution to make the solution acidic, then,
20 12.8 g of phenyltriethoxysilane was added, and the mixture was stirred for 30 minutes at 20°C. Then, 48 g of methyltri-
ethoxysilane was added and the mixture was stirred for 10 minutes to dissolve the ingredient.

2) Addition of core material and emulsification

25 [0293] The reaction solution prepared in the process 1) was controlled to pH 7.0 with 25% of aqueous sodium hydroxide solution, then, immediately, 100g of 2-ethylhexyl p-methoxycinnamate was added to the solution with stirring at 600 rpm to obtain an emulsion.

3) Micronization

30 [0294] The reaction solution prepared in the process 2) was stirred at 20°C for 10 minutes and diluted with 60g of water. Then, it was treated by the homomixer at 40°C and 6000 rpm for 60 minutes to micronize the components.

4) Prevention of coagulation and curing treatment of capsule wall

35 [0295] 1.0 g of hexaethyldisilazane was added to the emulsion prepared in the process 3) with stirring and keeping the emulsion at 40°C, then, 1.0 g of a 25% aqueous sodium hydroxide solution was added to control the pH at 7.0. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the solution was further heated to reflux with stirring for 6 hours. This reaction solution was cooled to obtain a microcapsule
40 containing core material.

5) Removal of gelatin and free 2-ethylhexyl p-methoxycinnamate

45 [0296] The dispersion obtained in the process 4) was separated by a centrifugal separator, the supernatant was discarded, and the remaining solution was washed by adding 100 ml of water. The same operation was repeated five times, gelatin and free 2-ethylhexyl p-methoxycinnamate were removed. Finally, 100 ml of water was added to the remainder to obtain a dispersion of a microcapsule containing core material.

[0297] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 1 and 5 giving the following results.

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55

Water dispersion of a capsule having a diameter from 1 to 30 μm , mainly from 10 to 20 μm	200 g
Components excepting water	50 %

[0298] In Example 9, a microcapsule containing core material of 2-ethylhexyl p-methoxycinnamate having a capsule wall made of organopolysiloxane composed of a hydrolysate poly-condensate of methyltriethoxysilane can be produced

in stable manner in a geatin solution.

- [0299] The microcapsule containing core material obtained in Example 9 was tested if the capsule thereof was broken according to the above-described Test method 1 or not, to find that a capsule having a particle size of about 8 μm or more was broken. Particularly, in the condition wherein capsules having a particle size from 8 to 15 μm were broken, 5 leaking of the core material out of the capsule was observed, and it was observed that the capsule wall and the core material are rounded respectively to form the shape of an "eight". However very little breakage was observed of a capsule having a particle size of less than 8 μm .

Example 10

- 10 Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen, methyltriethoxysilane and phenyltriethoxysilane

15 1) Preparation of prepolymer of capsule wall

- [0300] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 135 g of water, 15 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen (number-average 20 molecular weight of the hydrolyzed collagen is about 2000) and 3.6 g of 18% hydrochloric acid, and a mixture of 45.9 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.) and 12.4 g of phenyltriethoxysilane (KBE-103 manufactured by Shin-Etsu Silicone Co., Ltd.) was dropped from the dropping funnel at 50°C with stirring. [0301] The mixture was further stirred for 6 hours at 50°C. Then, 2.9 g of a 25% aqueous sodium hydroxide solution was added dropwise with stirring, to control the pH to 7.0.

25 2) Addition of core material and emulsification

- [0302] A mixture of 389 g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.) and 3.9 g of AZ-6101 ($\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_\alpha[\text{MeSi}(\text{EtO})\text{O}]_\beta\text{SiMe}_3$, manufactured by Nippon Unicar Co., Ltd.) was added to the 30 reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

3) Micronization

- 35 [0303] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes, to micronize the components.

4) Prevention of coagulation and curing treatment of capsule wall

- 40 [0304] 3.0 g of trimethylchlorosilane (KA-31, manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the solution prepared in the process 3) in the original reaction vessel with stirring at 250 rpm and 50°C, then, 4.4 g of a 25% aqueous sodium hydroxide solution was added dropwise immediately. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 2 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing a core material.

[0305] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 1.58%.

Example 11

- 50 [0306] A microcapsule containing a core material was produced in the same manner as in Examples 10 except that a mixture of 389 g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.) and 3.9 g of methylhydrogenpolysiloxane (KF-99P, manufactured by Shin-Etsu Silicone Co., Ltd.) was used instead of a mixture of 389 g of 2-ethylhexyl p-methoxycinnamate and 3.9 g of AZ-6101 ($\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_\alpha[\text{MeSi}(\text{EtO})\text{O}]_\beta\text{SiMe}_3$, manufactured by Nippon Unicar Co., Ltd.).

55 [0307] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 1.55%.

Example 12

[0308] A microcapsule containing a core material was produced in the same manner as in Examples 10 except that a mixture of 389 g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.) and 3.9 g of tetraethoxysilane (KBE-04, manufactured by Shin-Etsu Silicone Co., Ltd.) was used instead of a mixture of 389 g of 2-ethylhexyl p-methoxycinnamate and 3.9 g of AZ-6101 $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_\alpha[\text{MeSi}(\text{EtO})\text{O}]_\beta\text{SiMe}_3$, manufactured by Nippon Unicar Co., Ltd.).

[0309] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 1.05%.

Example 13

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen, methyltriethoxysilane, phenyltriethoxysilane and tetraethoxysilane

1) Preparation of prepolymer of capsule wall

[0310] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 135 g of water, 15 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen (number-average molecular weight of the hydrolyzed collagen is about 2000) and 3.6 g of 18% hydrochloric acid, and a mixture of 45.9 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.), 12.4 g of phenyltriethoxysilane (KBE-103 manufactured by Shin-Etsu Silicone Co., Ltd.) and 3.6g of tetraethoxysilane (KBE-04 manufactured by Shin-Etsu Silicone Co., Ltd.) was dropped from the dropping funnel at 50°C with stirring.

[0311] The mixture was further stirred for 6 hours at 50°C. Then, 2.9 g of a 25% aqueous sodium hydroxide solution was added dropwise with stirring, to control the pH to 7.0.

2) Addition of core material and emulsification

[0312] A mixture of 389 g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.) and 3.9 g of tetraethoxysilane (KBE-04 manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

3) Micronization

[0313] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes, to micronize the components.

4) Over coat treatment of capsule wall

[0314] A mixture of 1.28 g of methyltrichlorosilane (KA-13 manufactured by Shin-Etsu Silicone Co., Ltd.) and 6.0 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the reaction solution prepared in the process 3) in the original reaction vessel with stirring at 50°C and 250 rpm, and further, the mixture was stirred for 1 hour at 250 rpm. Then 4.05 g of a 25% aqueous sodium hydroxide solution was added for neutralization.

[0315] 30 minutes after the neutralization, the same operation was repeated.

5) Prevention of coagulation and curing treatment of capsule wall

[0316] 3.0 g of trimethylchlorosilane (KA-31, manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the solution prepared in the process 4) in the original reaction vessel with stirring at 250 rpm and 50°C, then, 4.4g of a 25% aqueous sodium hydroxide solution was added dropwise immediately. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 2 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing a core material.

[0317] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.20%.

Example 13A

- [0317] A microcapsule containing a core material was produced in the same manner as in Examples 13 except that tetraethoxysilane was not used.
- 5 [0318] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 2.36%.

Example 14

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and tetraethylsilane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed sericin, methyltriethoxysilane, phenyltriethoxysilane and tetraethoxysilane

1) Preparation of prepolymer of capsule wall

- 15 [0319] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 115.2 g of water, 12.8 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed sericin (number-average molecular weight of the hydrolyzed sericin is about 2000) and 5.0 g of 18% hydrochloric acid, and a mixture of 27.0 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.), 7.3 g of phenyltriethoxysilane (KBE-20 103 manufactured by Shin-Etsu Silicone Co., Ltd.) and 2.1g of tetraethoxysilane was dropped from the dropping funnel at 50°C with stirring.
- [0320] The mixture was further stirred for 5 hours at 50°C. Then, 4.4g of a 25% aqueous sodium hydroxide solution was added dropwise with stirring, to control the pH to 7.0.

25 2) Addition of core material and emulsification

- [0321] A mixture of 244g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.) and 2.44g of tetraethoxysilane (KBE-04 manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the reaction solution prepared in the process 1), which was cooled to 20°C, with stirring at 700 rpm, and the mixture was further stirred for 4 hours at 700 rpm.

3) Micronization

- 35 [0322] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 5000 rpm for 60 minutes, to micronize the components.

4) Over coat treatment of capsule wall

- 40 [0323] A mixture of 0.76 g of methyltrichlorosilane (KA-13 manufactured by Shin-Etsu Silicone Co., Ltd.) and 3.6 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the reaction solution prepared in the process 3) in the original reaction vessel with stirring at 50°C and 350 rpm. Then 5.0 g of a 25% aqueous sodium hydroxide solution was added.

5) Prevention of coagulation and curing treatment of capsule wall

- 45 [0324] 1.1 g of trimethylchlorosilane (KA-31, manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the solution prepared in the process 4) in the original reaction vessel with stirring at 400 rpm and 50°C, then, 2.3 g of a 25% aqueous sodium hydroxide solution was added dropwise after stirring for 1 hour. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 250 rpm for 2 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing core material.

[0325] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.16%.

[0326] After leaving this dispersion for 1 day, the amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was measured and it was 0.63%.

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Example 15

- [0327] A microcapsule containing core material was produced in the same manner as in Examples 14 except that

2.44g of tetraethoxysilane (KBE-04, manufactured by Shin-Etsu Silicone Co., Ltd.) was not added.

[0328] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 1.35%.

[0329] After leaving this dispersion for 1 day, the amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was measured and it was 1.61%.

5

Example 16

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and tetraethylsilane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed sericin, methyltriethoxysilane, hexyltrimethoxysilane and tetraethoxysilane

[0330] A microcapsule containing core material was produced in the same manner as in Examples 14 except that the amounts of 2-ethylhexyl p-methoxycinnamate and tetraethylsilane, added as the core materials, were changed to 266g and 2.66g, respectively; 7.3g of phenyltriethoxysilane was replaced with 6.3g of hexyltrimethoxysilane (KBM-3063C, manufactured by Shin-Etsu Silicone Co., Ltd.); and the amounts of the 25% aqueous sodium hydroxide solution were changed from 4.4g, 5.0g and 2.3g to 5.4g, 4.8g and 3.6g, respectively.

[0331] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.38%.

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Example 17

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[0332] A microcapsule containing core material was produced in the same manner as in Examples 16 except that 2.44g of tetraethoxysilane (KBE-04, manufactured by Shin-Etsu Silicone Co., Ltd.) was not added to the core material.

[0333] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 1.34%.

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Example 18

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Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and tetraethylsilane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen, methyltriethoxysilane, phenyltriethoxysilane and tetraethylsilane

30

1) Preparation of prepolymer of capsule wall

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[0334] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged 180 g of water, 20 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen (number-average molecular weight of the hydrolyzed collagen is about 2000) and 4.8 g of 18% hydrochloric acid, and a mixture of 61.2 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.), 16.5 g of phenyltriethoxysilane (KBE-103 manufactured by Shin-Etsu Silicone Co., Ltd.) and 4.8g of tetraethoxysilane was dropped from the dropping funnel at 50°C with stirring.

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[0335] The mixture was further stirred for 4 hours at 50°C. Then, 3.8 g of a 25% aqueous sodium hydroxide solution was added dropwise with stirring, to control the pH to 7.0.

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2) Addition of core material and emulsification

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[0336] A mixture of 69.7 g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.) and 0.697 g of tetraethoxysilane (KBE-04 manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the reaction solution prepared in the process 1) with stirring at 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

55

3) Micronization

[0337] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes, to micronize the components.

60

4) Overcoat treatment

65

[0338] A mixture of 1.7g of methyltrichlorosilane (KA-13, manufactured by Shin-Etsu Silicone Co., Ltd.) and 8.15g of methyltriethoxysilane (KBE-13, manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the solution prepared in the process 3) in the original reaction vessel with stirring at 250 rpm and 50°C. After stirring for one hour, 5.46 g of a 25%

aqueous sodium hydroxide solution was added dropwise.

[0339] After stirring further 30 minutes, a mixture of 1.7g of methyltrichlorosilane (KA-13, manufactured by Shin-Etsu Silicone Co., Ltd.) and 8.15g of methyltriethoxysilane (KBE-13, manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the resulting solution, once more. Thereafter, the resulting solution was stirred for one more hour, then 5.46 g of a 25% aqueous sodium hydroxide solution was added dropwise.

5) Prevention of coagulation and curing treatment of capsule wall

[0340] 5.0 g of trimethylchlorosilane (KA-31, manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the solution prepared in the process 4) in the original reaction vessel with stirring at 600 rpm and 50°C, then, 7.36 g of a 25% aqueous sodium hydroxide solution was added dropwise after stirring for 1 hour. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 250 rpm for 2 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing core material.

[0341] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.06%.

[0342] After leaving this dispersion for 1 day, the amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was measured and it was 0.39%.

Example 19

[0343] A microcapsule containing core material was produced in the same manner as in Examples 18 except that 0.697g of tetraethoxysilane (KBE-04, manufactured by Shin-Etsu Silicone Co., Ltd.) was not added.

[0344] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.13%.

[0345] After leaving this dispersion for 1 day, the amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was measured and it was 0.77%.

Example 20

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and tetraethylsilane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed collagen, methyltriethoxysilane, hexyltrimethoxysilane and tetraethoxysilane

[0346] A microcapsule containing core material was produced in the same manner as in Examples 18 except that the amounts of 2-ethylhexyl p-methoxycinnamate and tetraethylsilane, added as the core materials, were changed to 70.3g and 0.703g, respectively; and 16.5g of phenyltriethoxysilane was replaced with 14.15g of hexyltrimethoxysilane.

[0347] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.13%.

[0348] After leaving this dispersion for 1 day, the amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was measured and it was 0.63%.

Example 21

[0349] A microcapsule containing core material was produced in the same manner as in Examples 20 except that 0.703g of tetraethoxysilane (KBE-04, manufactured by Shin-Etsu Silicone Co., Ltd.) was not added to the core material.

[0350] The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.15%.

[0351] After leaving this dispersion for 1 day, the amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was measured and it was 1.00%.

Analysis method 7

[0352] 0.1 g of the resulting dispersion of the microcapsule containing core material is weighed into a screw tumber having a diameter of 27 mm and a height of 55 mm, and about 5 mL of water is added. To this is added 10 mL of n-hexane and the tube is capped, the center portion is immediately fixed in a horizontal direction and is allowed to rotate with the rotation symmetry axis kept vertical using a motor at 150 rpm, to extract free 2-ethylhexyl p-methoxycinnamate. After rotation for 2 minutes, 100 μ L of a hexane layer is transferred into a 10 ml measuring flask by a micropipette, and n-hexane is added to a weighing line. This is called sample A. The tumber is further rotated for 2 minutes and the same treatment is conducted. This is called sample B. The concentration of 2-ethylhexyl p-methoxycinnamate of the sample A and the sample B is measured using liquid chromatography. If the measurement result of the sample A is named a and the measurement result of the sample B is named b, the difference between the analysis result b and the analysis

result a (b-a) can be regarded as bleeding amount over 2 minutes. The measurement result a also include the bleeding amount over 2 minutes, i.e. (b-a), together with the amount of free portion, therefore, a-(b-a) can be regarded as the amount of the free 2-ethylhexyl p-methoxycinnamate.

5 Example 22

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and tetraethylsilane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed sericin, methyltriethoxysilane, phenyltriethoxysilane and tetraethoxysilane

10 1) Preparation of prepolymer of capsule wall

[0353] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged with 90 g of water, 10 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed sericin (number-average molecular weight of the hydrolyzed sericin is about 2000) and 3.6 g of 18% hydrochloric acid, and a mixture of 24 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.), 6.45 g of phenyltriethoxysilane (KBE-103 manufactured by Shin-Etsu Silicone Co., Ltd.) and 1.86g of tetraethoxysilane was dropped from the dropping funnel at 50°C with stirring.

20 [0354] The mixture was further stirred for 4 hours at 50°C, then cooled to 20°C. Then, 2.45g of a 25% aqueous sodium hydroxide solution was added dropwise with stirring, to control the pH to 7.0.

2) Addition of core material and emulsification

25 [0355] After stirring the reaction solution prepared in the process 1) for 30 minutes, a mixture of 257.4g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.) and 2.6g of tetraethoxysilane (KBE-04 manufactured by Shin-Etsu Silicone Co., Ltd.) was added thereto with stirring at 20°C and 600 rpm, and the mixture was further stirred for 4 hours at 600 rpm.

30 3) Micronization

[0356] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes. Then, the resulting solution was trasfered to the original reaction vessel and stirred at 50°C and 600 rpm for 14 hours. Thereafter, the resulting mixture was transferred to the vessel of a homomixer again and treated by the homomixer at 50°C and 6000 rpm for 60 minutes to micronize the components.

4) Over coat treatment of capsule wall

40 [0357] A mixture of 0.67 g of methyltrichlorosilane (KA-13 manufactured by Shin-Etsu Silicone Co., Ltd.) and 3.2 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the reaction solution prepared in the process 3) in the original reaction vessel with stirring at 50°C and 250 rpm and the resulting mixture was stirred at 250 rpm for 1 more hour. Then 2.2g of a 25% aqueous sodium hydroxide solution was added for neutralization.

45 5) Prevention of coagulation and curing treatment of capsule wall

[0358] 2.0 g of trimethylchlorosilane (KA-31, manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the solution prepared in the process 4) with stirring at 250 rpm and 50°C, then, 2.8 g of a 25% aqueous sodium hydroxide solution was added dropwise after stirring for 1 hour. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 2 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule containing core material.

[0359] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

55 [0360] Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 3 µm
The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 1.686%.

The amount of 2-ethylhexyl p-methoxycinnamate which leaked in 2 minutes was 0.1138%.

Example 22A

[0361] A microcapsule containing core material was produced in the same manner as in Example 22 except that the prepolymer was prepared without using tetraethoxysilane.

5 [0362] Water dispersion of a capsule having a diameter from 1 to 5 µm.

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.210%.

The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.0348%/minute.

Example 23

10

1)

[0363] The processes, "Preparation of prepolymer of capsule wall" and "Addition of core material and emulsification", were conducted in the same manner as in Example 22.

15

2) Micronization

20

[0364] The reaction solution prepared in the process 1) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes.

25

3)

[0365] The processes, "Over coat treatment of capsule wall" and "Prevention of coagulation and curing treatment of capsule wall", were conducted in the same manner as in Examples 22 to obtain a microcapsule containing core material.

[0366] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

[0367] Water dispersion of a capsule having a diameter from 0.3 to 5 µm, mainly from 1 to 3 µm
The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.7767%.

30

The amount of 2-ethylhexyl p-methoxycinnamate which leaked in 2 minutes was 0.3801%.

Example 24

1) Preparation of prepolymer of capsule wall

35

[0368] The process, "Preparation of prepolymer of capsule wall", was conducted in the same manner as in Example 22 except that the amounts of methyltriethoxysilane, phenyltriethoxysilane, tetraethylsilane and 25% aqueous sodium hydroxide solution were changed to 21.6g, 5.73g, 1.67g and 2.2g, respectively. Since the amount of the 25% aqueous sodium hydroxide solution was 2.2g, the pH of the resulting solution was not controlled at 7.0.

40

2) Addition of core material and emulsification

45

[0369] The process, "Addition of core material and emulsification", was conducted in the same manner as in Example 22, except that the amounts of 2-ethylhexyl p-methoxycinnamate and tetraethylsilane were changed to 228.2g and 2.3g, respectively.

3) Micronization

50

[0370] Micronization was conducted about the reaction solution prepared in the process 2) in the same manner as in Example 22.

4) Over coat treatment of capsule wall

55

[0371] 0.25g of a 25% aqueous sodium hydroxide solution was dropwise added to the reaction solution prepared in the process 3) with stirring at 50°C and 250 rpm. Then, a mixture of 0.585 g of methyltrichlorosilane (KA-13 manufactured by Shin-Etsu Silicone Co., Ltd.) and 2.78 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.) was added thereto and the resulting mixture was stirred for 1 more hour. Thereto, 1.9g of a 25% aqueous sodium hydroxide solution was added for neutralization.

5) Prevention of coagulation and curing treatment of capsule wall

"Prevention of coagulation and curing treatment of capsule wall" was conducted about the reaction solution prepared in the process 4) in the same manner as in Example 22, except that the amounts of trimethylchlorosilane and 25% aqueous sodium hydroxide solution were changed to 1.2g and 1.7g, respectively to obtain a microcapsule containing core material.

[0372] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

10

15	Water dispersion of a capsule having a diameter from 1 to 5 µm. Components excepting water	64.7 %
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The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.818%.
The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.0551%/minute.

20 Example 25

1) Preparation of prepolymer of capsule wall

[0373] The process, "Preparation of prepolymer of capsule wall", was conducted in the same manner as in Example 22 except that tetraethoxysilane was not added and 4.0g of propylene glycol was added after the pH was controlled to 7.0.

2) Addition of core material and emulsification

[0374] The process, "Addition of core material and emulsification", was conducted in the same manner as in Example 22, except that the amounts of 2-ethylhexyl p-methoxycinnamate and tetraethylsilane were changed to 250g and 2.5g, respectively.

3) Micronization

[0375] Micronization was conducted about the reaction solution prepared in the process 2) in the same manner as in Example 22, except that the rotation speed of the homomixer was changed to 8000rpm.

4)

[0376] The processes, "Over coat treatment of capsule wall" and "Prevention of coagulation and curing treatment of capsule wall", were conducted about the reaction solution prepared in the process 3) in the same manner as in Example 22 to obtain a microcapsule containing core material.

[0377] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

[0378] Water dispersion of a capsule having a diameter from 0.3 to 3 µm, mainly from 1 to 3 µm.

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.7994%.

The amount of 2-ethylhexyl p-methoxycinnamate which leaked in 2 minutes was 0.2722%.

50 Example 26

[0379] A microcapsule containing core material was produced in the same manner as in Example 25 except that 4.0g of propylene glycol was replaced with 4.0g of glycerin.

[0380] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

Water dispersion of a capsule having a diameter from 0.3 to 3 µm, mainly from 1 to 3 µm.

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.7028%.

The amount of 2-ethylhexyl p-methoxycinnamate which leaked in 2 minutes was 0.0219%.

Example 27

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and tetraethylsilane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed sericin, methyltriethoxysilane and octyltriethoxysilane

[0381] A microcapsule containing core material was produced in the same manner as in Example 25 except that 6.45g of phenyltriethoxysilane was replaced with 7.5g of octyltriethoxysilane (A-137 manufactured by Nippon UniCar Co., Ltd.).

[0382] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

Water dispersion of a capsule having a diameter from 0.3 to 3 μm , mainly from 1 to 3 μm .

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.4925%.

The amount of 2-ethylhexyl p-methoxycinnamate which leaked in 2 minutes was 0.0695%.

15

Example 28

Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and 4-tert-butyl-4'-methoxydibenzoylmethane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed sericin, methyltriethoxysilane and phenyltriethoxysilane

1) Preparation of prepolymer of capsule wall

[0383] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm equipped with a mechanical stirrer, having an upper cover equipped with a dropping funnel and a reflux condenser, was previously charged with 90 g of water, 10 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed sericin (number-average molecular weight of the hydrolyzed sericin is about 2000) and 4.0 g of 18% hydrochloric acid, and a mixture of 24.3 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.) and 6.6 g of phenyltriethoxysilane (KBE-103 manufactured by Shin-Etsu Silicone Co., Ltd.) was dropped from the dropping funnel at 50°C with stirring.

[0384] The mixture was further stirred for 4 hours at 50°C, then, 4.0g of a 20% aqueous sodium hydroxide solution and 1.0g of EDTA-2Na dispersed in 40g of water were added dropwise with stirring, followed by addition of 20g of ethanol, to control the pH to 7.0.

2) Addition of core material, emulsification and Micronization

35

[0385] The reaction solution prepared in the process 1) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 9000 rpm for 90 minutes with dropwise adding a mixture of 203g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.), 50.8g of 4-tert-butyl-4'-methoxydibenzoylmethane (manufactured by Nippon Roche K.K.) and 2.5g of tetraethoxysilane (KBE-04 manufactured by Shin-Etsu Silicone Co., Ltd.), to micronize the components.

[0386] Then, the resulting solution was transferred to the original reaction vessel and stirred at 50°C and 600 rpm. Thereafter, the resulting mixture was transferred to the vessel of a homomixer again and treated by the homomixer at 50°C and 6000 rpm for 60 minutes to micronize the components.

45

3) Over coat treatment of capsule wall

[0387] A mixture of 0.68 g of methyltrichlorosilane (KA-13 manufactured by Shin-Etsu Silicone Co., Ltd.) and 3.24 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.) was dropwise added to the reaction solution prepared in the process 2) in the original reaction vessel with stirring at 50°C and 400 rpm and the resulting mixture was stirred for 1 more hour. Then 2.7g of a 20% aqueous sodium hydroxide solution was dropwise added.

5) Prevention of coagulation and curing treatment of capsule wall

[0388] 2.0 g of trimethylchlorosilane (KA-31, manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the solution prepared in the process 4) with stirring at 400 rpm and 50°C, then, 3.7 g of a 20% aqueous sodium hydroxide solution was added dropwise after stirring for 1 hour. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 400 rpm for 2 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a microcapsule

containing core material.

[0389] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

5

Water dispersion of a capsule having a diameter from 1 to 20 µm, mainly from 1 to 3 µm	436.0g
Components excepting water	60.72 %

10

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.5658%.
The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.0427%/minute.

Example 29

15

[0390] A microcapsule containing core material was produced in the same manner as in Examples 28 except that 20g of ethanol was replaced with 4.5g of glycerin.

[0391] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

20

Water dispersion of a capsule having a diameter from 1 to 10 µm, mainly from 1 to 3 µm	460g.
Components excepting water	60.13 %

25

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.5151%.
The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.0254%/minute.

Example 30

[0392] A microcapsule containing core material was produced in the same manner as in Examples 28 except that a mixture of 1.0g of EDTA-2Na dispersed in 40g of water and 4.5g of propyleneglycol was added instead of that of 1.0g of EDTA-2Na dispersed in 40g of water, then 20g of ethanol was added.

[0393] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

40

Water dispersion of a capsule having a diameter from 1 to 15 µm, mainly from 1 to 3 µm	466.2g.
Components excepting water	59.8%

45

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.1848%.
The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.0192%/minute.

Example 31

[0394] A microcapsule containing core material was produced in the same manner as in Examples 28 except that a mixture of 1.0g of EDTA-2Na dispersed in 40g of water and 4.5g of 1,3-buteneglycol was added instead of that 1.0g of EDTA-2Na dispersed in 40g of water, then 20g of ethanol was added.

[0395] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

55

Water dispersion of a capsule having a diameter from 1 to 20 µm, mainly from 1 to 3 µm	460.4g.
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(continued)

Components excepting water	60.7%
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- 5 The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.5317%.
The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.0391%/minute.

Example 32

- 10 [0396] A microcapsule containing core material was produced in the same manner as in Examples 28 except that the amounts of methyltriethoxysilane and phenyltriethoxysilane were changed to 16.2g and 4.4g, respectively.
[0397] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

15

Water dispersion of a capsule having a diameter from 1 to 10 µm, mainly from 1 to 3 µm	394.0g.
Components excepting water	58.4%

20

- The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.5477%.
The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.0088%/minute.

Example 33

25

- Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and 4-tert-butyl-4'-methoxydibenzoylmethane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed sericin, methyltriethoxysilane and octyltriethoxysilane

30

- [0398] A microcapsule containing core material was produced in the same manner as in Examples 30 except that 6.6g of phenyltriethoxysilane was replaced with 7.5g of octyltriethoxysilane (A-137 manufactured by Nippon UniCar Co., Ltd.).
[0399] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

35

Water dispersion of a capsule having a diameter from 1 to 15 µm	463.9g.
Components excepting water	60.27 %

- The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 1.5579%.
The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.3406%/minute.

45 Example 34

- 1) The processes, "1) Preparation of prepolymer of capsule wall" and "2) Addition of core material and emulsification", were conducted in the same manner as in Examples 30.

50 2) Addition of core material, emulsification and Micronization

- [0400] The reaction solution prepared in the process 1) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 9000 rpm for 90 minutes with dropwise adding a mixture of 203g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.), 50.8g of 4-tert-butyl-4'-methoxydibenzoylmethane (manufactured by Nippon Roche K.K.) and 2.5g of tetraethoxysilane (KBE-04 manufactured by Shin-Etsu Silicone Co., Ltd.) under a reduced pressure (500mmHg) to micronize the components.

[0401] Then, the resulting solution was transferred to the original reaction vessel and stirred at 50°C and 600 rpm. Thereafter, the resulting mixture was transferred to the vessel of homomixer again and treated by the homomixer at

50°C and at 6000 rpm for 60 minutes to micronize the components.

3)

5 [0402] The processes, "Over coat treatment of capsule wall" and "Prevention of coagulation and curing treatment of capsule wall", were conducted in the same manner as in Examples 30 to obtain a microcapsule containing core material.

[0403] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

10

15	Water dispersion of a capsule having a diameter from 1 to 20 µm, mainly from 1 to 3 µm Components excepting water	466.1g. 59.55 %
----	--	--------------------

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.5812%.

The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.1262%/minute

20 Example 35

1) A prepolymer was prepared in the same manner as in Example 30.

2) Addition, emulsification and micronization of core material

25

[0404] The reaction solution prepared in the process 1) was transferred to a vessel of a homomixer. Thereto, a mixture of 203 g of 2-ethylhexyl p-methoxycinnamate (MCX manufactured by Nippon Roche K.K.), 50.8 g of 4-tert-butyl-4'-methoxydibenzoylmethane (manufactured by Nippon Roche K.K.) and 2.5 g of tetraethoxysilane (KBE-04 manufactures by Shin-Etsu Silicon Co., Ltd) was added dropwise while the solution was being treated by the homomixer at 9000 rpm for 90 minutes in ultrasonic wave (200 W) at 50°C, to be micronized. Then, the reaction solution was stirred at 600 rpm at 50°C in the original reaction vessel. Then, the reaction solution was again transferred to the vessel of the homomixer, and treated by the homomixer at 6000 rpm and 50°C for 60 minutes to be micronized.

30

3) [0405] The processes, "Over coat treatment of capsule wall" and "Prevention of coagulation and curing treatment of capsule wall", were conducted in the same manner as in Examples 30 to obtain a microcapsule containing core material.

[0406] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

35

45	Water dispersion of a capsule having a diameter from 1 to 20 µm, mainly from 1 to 3 µm Components excepting water	445.9g. 60.48 %
----	--	--------------------

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.7385%.

The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.0147%/minute.

50

Example 36

1) Preparation of prepolymer of capsule wall

55 [0407] The process, "1) Preparation of prepolymer of capsule wall", was conducted in the same manner as in Examples 28 except that 2.4 g of tetraethoxysilane (KBE-04 manufactured by Shin-Etsu Silicone Co., Ltd.) was added and 20g of ethanol was not added after the pH was controlled to 7.0.

2) Addition of core material and emulsification

[0408] A mixture of 202.64g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.) and 50.66g of 4-tert-butyl-4'-methoxydibenzoylmethane (manufactured by Nippon Roche K.K.) was added to the reaction solution prepared in the process 1) with stirring at 600rpm, then the resulting solution was stirred at 600 rpm for 2 hours.

3) Micronization

[0409] The reaction solution prepared in the process 2) was transferred to the vessel of homomixer and treated by the homomixer at 50°C and 6000 rpm for 90 minutes. Then, the resulting solution was transferred to the original reaction vessel and stirred at 50°C and 600 rpm for 15 hours. Thereafter, the resulting mixture was transferred to the vessel of the homomixer again and treated by the homomixer at 50°C and 6000 rpm for 60 minutes to micronize the components.

4)

[0410] The processes, "Over coat treatment of capsule wall" and "Prevention of coagulation and curing treatment of capsule wall", were conducted in the same manner as in Examples 30 to obtain a microcapsule containing core material.

[0411] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

25	Water dispersion of a capsule having a diameter from 2 to 20 μm Components excepting water	59.36 %
----	--	---------

The amount of free 2-ethylhexyl p-methoxycinnamate in the dispersion was 0.9315%.

The leaking speed of 2-ethylhexyl p-methoxycinnamate was 0.3521%/minute.

30 Reference example 1

Production of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl sodium polyaspartate

35 [0412] A sodium polyaspartate solution (Aquadew SPA-30 manufactured by Ajinomono Co., Inc.) is electrically dialysed, then, the concentration is controlled to 20% and the pH was controlled at about 11 to prepare a solution for reaction.

[0413] The prepared solution is charged into a glass reaction vessel, heated at 60°C and stirred. When the reaction solution reaches 60°C, γ -glycidoxypolytrimethoxysilane (KBE-403 manufactured by Shin-Etsu Silicone Co., Ltd.) is 40 added dropwise from a dropping funnel and the mixture is stirred for 5 hours at 60°C (the amount of the γ -glycidoxypolytrimethoxysilane used is about 3.1 g per 100 g of the reaction solution).

[0414] The effective component concentration of the reacted compound is controlled to 15%.

Example 37

45 Production of a microcapsule containing 2-ethylhexyl p-methoxycinnamate and tetraethylsilane and having a capsule wall made of organopolysiloxane composed of a co-polycondensate of the hydrolysate of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl sodium polyaspartate, methyltriethoxysilane, phenyltriethoxysilane and tetraethoxysilane

50 1) Preparation of prepolymer of capsule wall

[0415] A 2-liter round bottom cylindrical glass reaction vessel having an internal diameter of 12 cm was previously charged 90 g of water, 10 g of N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl sodium polyaspartate (number-average molecular weight of the sodium polyaspartate is about 1000), obtained in Reference Example 1, and 10 g of 18% hydrochloric acid, and a mixture of 12.3 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.), 3.3 g of phenyltriethoxysilane (KBE-103 manufactured by Shin-Etsu Silicone Co., Ltd.) and 1.9g of tetraethoxysilane was dropped from the dropping funnel at 50°C with stirring.

[0416] The mixture was further stirred for 4 hours at 55°C, then cooled to 25°C. Then, 10g of a 20% aqueous sodium

hydroxide solution was added dropwise, to control the pH to 7.0.

2) Addition of core material and emulsification

- 5 [0417] A mixture of 160.7g of 2-ethylhexyl p-methoxycinnamate (MCX, manufactured by Nippon Roche K.K.) and 1.6g of tetraethoxysilane (KBE-04 manufactured by Shin-Etsu Silicone Co., Ltd.) was added thereto with stirring at 600 rpm, and the mixture was further stirred for 2 hours at 600 rpm.

10 3) Micronization

- [0418] The reaction solution prepared in the process 2) was transferred to a vessel of a homomixer, and treated by the homomixer at 50°C and 6000 rpm for 90 minutes to micronize the components.

15 4) Over coat treatment of capsule wall

- [0419] A mixture of 0.3 g of methyltrichlorosilane (KA-13 manufactured by Shin-Etsu Silicone Co., Ltd.) and 6 g of methyltriethoxysilane (KBE-13 manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the reaction solution prepared in the process 3) in the original reaction vessel with stirring at 50°C and 450 rpm and the resulting mixture was stirred at 450 rpm for 1 more hour. Then 0.4g of a 20% aqueous sodium hydroxide solution was added for neutralization.

20

5) Prevention of coagulation and curing treatment of capsule wall

- [0420] 0.5 g of trimethylchlorosilane (KA-31, manufactured by Shin-Etsu Silicone Co., Ltd.) was added to the solution prepared in the process 4) with stirring at 450 rpm and 50°C, then, 0.6g of a 20% aqueous sodium hydroxide solution was added dropwise after stirring at 450 rpm for 1 hour. The temperature of the reaction solution was raised gradually to reflux. A vapor containing alcohol was distilled off, and the remaining mixture was further heated to reflux with stirring at 150 rpm for 3 hours. This reaction solution was cooled with stirring at 150 rpm at room temperature to obtain a micro-capsule containing core material.

- 25 [0421] The dispersion of the resulting microcapsule containing core material was analyzed according to Analysis methods 5 and 7 giving the following results.

35

Water dispersion of a capsule having a diameter of 15 μm or smaller Components excepting water	50.50 %
---	---------

Analysis method 8

40

Measurement of SPF value and ultraviolet ray transmittance

- [0422] A measuring sample was applied on a surgical tape (TRANSPORÉ TAPE, manufactured by 3M Corp.), this was irradiated with a ultraviolet ray, and the amount of the transmitted light was measured by a SPF analyzer, (UV-1000S, manufactured by LABSPHERE Corp., US). The numerical value in the examples is an average of 40 values. The amount of the sample applied on a surgical tape is 2 μl/cm² and a certain amount when measuring SPF value and ultraviolet ray transmittance, respectively.

45 [0423] Calculation of SPF value

50

$$\text{SPF} = \frac{\sum_{290\text{nm}}^{400\text{nm}} E(\lambda)\epsilon(\lambda)}{\sum_{290\text{nm}}^{400\text{nm}} (E(\lambda)\epsilon(\lambda)) / (\text{MPF}(\lambda))}$$

55

E(λ): Spectral distribution of day light

ε (λ): Action spectrum of delayed type actinic erythema

MPF (λ): Reciprocal of transmittance at each wavelength

Analysis method 9

Measurement of skin permeability

5 [0424] Yucatan Micropig skin (5 months old, male, Nippon Charsliver) frozen and stored at -80°C was thawed at room temperature over 30 minutes, effluent fat adhered to skin was removed, then, the skin was cut into 2 cm square and used for measurement. A sample was applied to thus obtained skin and subjected to permeation test.

10 [0425] The permeation test was conducted using an improved Franz type diffusion cell (area on which a preparation is applied is 1.1 cm², receptor phase: 16 ml). 0.1 ml of the prepared sample was placed into the donor phase, and kept at 37°C for 24 hours. After 24 hours, the sample on the surface of the skin was cleanly removed by purified water, then, separated to epidermis and hypodermis. They were homogenized with 5 ml of MeOH, when, centrifugally separated (3000 rpm, 30 minutes), and the supernatant was separated and filtrated through a membrane filter (Cellulose Acetate 0.80 µm ADAVANTEC TOYO). Then, the concentration of the ultraviolet ray absorber was measured by HPLC.

15 [Measuring condition of HPLC]

[0426]

HPLC: Shimadzu LC-6A system (manufactured by Shimadzu Corp.)
 20 Column: TSK-GEL ODS-120T 4.6 mm 150mm (manufactured by Tosoh Corp.)
 Mobile phase : methanol:water = 9:1
 Flow rate: 1.0 ml/min
 Detector: Ultraviolet spectrophotometer SPD-6A (manufactured by Shimadzu Corp.)
 Detection wavelength: 310 nm

25 Example 38

[0427] Ultraviolet ray transmittance at wave-length of 310nm of samples obtained in Examples 22A, 24 and 28 and 2-ethylhexyl p-methoxycinnamate were measured according to Analysis method 8, and the results are shown in the following Table.

	Example 22A	Example 24	Example 28	2-ethylhexyl p-methoxy-cinnamate
Applied amount 1 *1	54.1	61.1	64.5	72.2
Applied amount 2 *2	48.7	54.5	58.1	72.2
Ultraviolet ray transmittance	1.7	1.0	1.75	2.2

*1 Applied amount 1 : amount(mg) of the applied sample after dried on 80cm² of the Tape

*2 Applied amount 2 : amount (mg) of ultraviolet ray absorber contained in the applied sample on 80cm² of the Tape

45 [0428] Although the amounts of the applied samples obtained in Examples 22A, 24 and 28 are less than the amount of the applied 2-ethylhexyl p-methoxy-cinnamate, ultraviolet ray transmittance of the Examples 22A, 24 and 28 are smaller than that of 2-ethylhexyl p-methoxy-cinnamate.

50 Example 39

[0429] Skin permeability of a microcapsule obtained in Examples 28 and 50% by weight of isopropylmiristate solution of 2-ethylhexyl p-methoxycinnamate were measured according to Analysis method 9, and the results are shown in the following Table.

	Concentration in epidermis ($\mu\text{g}/\text{cm}^3$)	Concentration in hypodermis ($\mu\text{g}/\text{cm}^3$)
Microcapsule obtained in Examples 28	5	1700
2-Ethylhexyl p-methoxycinnamate/ isopropyl miristate solution	52	12000

[0430] It was recognized that the microcapsule obtained in Examples 28 repress permeation into skin of a ultraviolet ray absorber contained in the capsule.

15 Example 40, Comparative Example 4: Livid Foundation

[0431] Stearic acid, beeswax, hydrogenated lanolin, isopropyl isostearate, squalane and sorbitan sesquioleate were weighed, and dissolved at 80°C (Solution 1). Separately, triethanolamine, 1,3-butylene glycol, partial purified water and the microcapsule containing core material obtained in the Example 13 were weighed, and heated to 85°C and added to Solution 1 gradually with stirring. After cooling to 45°C, a perfume was added and cooled to about 40°C (Solution 2).

[0432] Separately, titanium oxide, zinc oxide, kaolin, talc and iron oxide were weighed and to this was added the remaining purified water. The mixture was dispersed completely in a homomixer, then, Solution 2 was added thereto and the mixture was further stirred and dispersed thoroughly to obtain a sample for Example 40.

[0433] A sample for Comparative Example 4 was obtained in the same manner except 2-ethylhexyl p-methoxycinnamate was used instead of the microcapsule containing core material.

[0434] The amount of 2-ethylhexyl p-methoxycinnamate, a ultraviolet ray absorber, contained in the microcapsule used in the Example is same to that of the ultraviolet ray absorber compounded in the Comparative example. This will also be applied to the following examples and comparative examples.

[0435] Any of the amounts compounded of components in the examples and comparative examples is by weight, and when the amount compounded is not amount of a solid component, the concentration of the solid component is described in parenthesis following the component name. This will also be applied to the following examples and comparative examples.

35

		Amount compounded (W/W%)	
		Example 40	Comparative example 4
40	1 Titanium oxide	0.60	0.60
40	2 Zinc oxide	2.00	2.00
45	3 Kaolin	3.00	3.00
45	4 Talc	4.00	4.00
50	5 Iron oxide	1.00	1.00
50	6 Stearic acid	2.00	2.00
55	7 Beeswax	1.20	1.20
55	8 Hydrogenated lanolin	1.00	1.00
55	9 Isopropyl isostearate	2.00	2.00
55	10 Squalane	2.00	2.00
55	11 Sorbitan sesquioleate	0.40	0.40
55	12 Triethanolamine	0.50	0.50
55	13 1,3-Butylene glycol	2.80	2.80
55	14 Lecithin	0.20	0.20

(continued)

		Amount compounded (W/W%)	
		Example 40	Comparative example 4
5	15 Preservative	0.30	0.30
	16 Perfume	0.50	0.50
	17 Purified water	to make 100	to make 100
10	A Microcapsule	62.60	-
	B 2-Ethylhexyl p-methoxycinnamate	-	30.00

[0436] SPF value of the resulting liquid foundation was measured by Analysis method 8, and the results are shown below.

	SPF value
20	Example 40 20.8
	Comparative example 4 18.8

[0437] The appearance immediately after preparation and three months are shown below

	Appearance(directly after preparation)	Appearance (after three months)
30	Example 40 Uniform	Uniform
	Comparative example 4 Uniform	Coagulated, Separated

[0438] The liquid foundation of Example 40 was superior to that of Comparative Example 4 in effect for preventing a ultraviolet ray. In spite of a large amount of 2-ethylhexyl p-methoxycinnamate compounded, coagulation and separation with the lapse of time did not occur, that is, stability was excellent. Further, when the liquid foundation of Example 40 was applied to skin, oil feeling was little and tackiness was repressed.

40 Example 41, Comparative Example 5

[0439] Solid foundations having the following formulations were obtained in analogous manners as in Example 40 and Comparative Example 4 using a microcapsule containing core material obtained in Example 22A.

45

		Amount compounded (W/W%)	
		Example 41	Comparative example 5
50	1 Titanium oxide	20.00	20.00
	2 Zinc oxide	3.00	3.00
	3 Kaolin	6.00	6.00
55	4 Talc	8.00	8.00
	5 Iron oxide	4.00	4.00

(continued)

		Amount compounded (W/W%)	
		Example 41	Comparative example 5
5	6 Beeswax	8.40	8.40
10	7 Polyoxyethylene curing castor oil	0.60	0.60
15	8 Carnauba wax	1.20	1.20
20	9 Olive oil	13.50	13.50
	10 Purified castor oil	6.00	6.00
	11 Sodium oleylphosphate	0.60	0.60
	12 Preservative	0.30	0.30
	13 Perfume	0.30	0.30
	14 Octyldodecanol	to make 100	to make 100
	A Microcapsule	16.5	-
	B 2-Ethylhexyl p-methoxycinnamate	-	10.00

[0440] SPF value of a sample prepared by diluting the resulting solid foundation by 4-fold with octyldodecanol was measured by Analysis method 8, and the results are shown below.

25

	SPF value
	Example 41 16.7
30	Comparative example 5 14.0

[0441] The product was applied in an amount of 0.5 g on the back of hand, and "adhesion to skin" was evaluated by 10 panelists, the results are shown below.

35

Evaluation of adhesion		
Number of panelists who decided the product of Example 41 good		7
Number of panelists who decided the product of Comparative Example 5 good		3

[0442] The solid foundation of Example 41 was superior to that of Comparative Example 5 in adhesion onto skin.

45

Example 42, Comparative Example 6

[0443] Sunscreen lotions having the following formulations were obtained in analogous manners as in Example 40 and Comparative Example 4 using a microcapsule containing core material obtained in Example 36.

50

		Amount compounded (W/W%)	
		Example 42	Comparative example 6
55	1 Alkyl acrylate-alkyl methacrylate-polyoxyethylene (20) stearyl ether copolymerized emulsion (30%)	0.60	0.60

(continued)

		Amount compounded (W/W%)	
		Example 42	Comparative example 6
5	2	Hydroxyethyl-cellulose	0.30
	3	Purified water	20.00
	4	Sodium hydroxide (1% aqueous solution)	3.00
10	5	Purified water	20.00
	6	Propylene glycol	8.00
	7	EDTA-2Na	0.20
15	8	Preservative	0.30
	9	Purified water	to make 100.00
	A	Microcapsule	9.4
	B	2-Ethylhexyl p-methoxycinnamate	-
20	C	4-tert-Butyl-4'-methoxydibenzoyl	1.00

[0444] The resulting sunscreen lotion could not easily form a uniform coating when used in small amount, therefore, double amount ($4 \mu\text{l}/\text{cm}^2$) based on usual was used for the test. SPF value, UVA transmittance and UVB transmittance obtained by Analysis method 8 are shown below.

25

30

	SPF value	UVA transmittance (%)	UVB transmittance (%)
	Example 42	10.7	33.1
	Comparative example 6	7.7	43.6

[0445] From the above-described results, it is apparent that the sunscreen lotion of Example 42 is excellent in ultraviolet ray preventing effect.

[0446] Appearance immediately after preparation and after three months are shown below.

40

45

	Appearance (immediately after preparation) uniform	Appearance (after three months) uniform
	Example 42	emulsification rough
	Comparative example 6	emulsification and semitransparent

[0447] As a result of observation of change with the lapse of time, the product of Example 42 can be compounded stably even in a formulation system in which an active agent is not compounded as described above.

50 Example 43, Comparative Example 7

[0448] Sunscreen creams having the following formulations were obtained in analogous manners as in Example 40 and Comparative Example 4 using a microcapsule containing core material obtained in Example 36.

55

		Amount compounded (W/W%)	
		Example 43	Comparative example 7
1	Alkyl acrylate-alkyl methacrylate-polyoxyethylene (20) stearyl ether copolymer emulsion (30%)*1	1.00	1.00
2	Carboxyvinyl polymer *2(1% aqueous solution)	50.00	50.00
3	Cetostearyl 2-ethylhexanoate (2)	5.00	5.00
4	Concentrated glycerin	3.00	3.00
5	EDTA-2Na	0.20	0.20
6	Preservative	0.20	0.20
7	Triethanolamine	1.30	1.30
8	Purified water	10.00	10.00
9	Purified water	to make 100.0	to make 100.0
A	Microcapsule	18.7	-
B	2-Ethylhexyl p-methoxycinnamate	-	8.00
C	4-tert-Butyl-4'-methoxydibenzoyl		2.00

*1 Aculyn 22 (manufactured by ROHM and HAAS)

*2 Carbopole 940 (manufactured by The BF Goodrich Company)

[0449] SPF value, UVA transmittance and UVB transmittance of the resulting sunscreen cream are shown below. In Comparative Example 7, the product was separated and not uniform, therefore, sampling was effected immediately after intense stirring and the resulting samples were subjected to the tests.

	SPF value	UVA transmittance (%)	UVB transmittance (%)
Example 43	4.7	50.9	19.0
Comparative example 7	3.8	56.2	23.7

[0450] Appearance immediately after preparation and after three months are shown below.

	Appearance (immediately after preparation) uniform	Appearance (after three months) uniform
Example 43	emulsification	emulsification
Comparative example 7	separated	separated

[0451] As is known from the above-described results, microcapsule of the instant invention can be easily compounded in a formulation, and is excellent in stability with the lapse of time. Therefore, compounding of a ultraviolet ray absorber became possible even in cosmetics in which compounding of a ultraviolet ray absorber has been conventionally difficult.

Example 44, Comparative Example 8

[0452] Milky lotions having the following formulations were obtained in analogous manners as in Example 40 and Comparative Example 4 using a microcapsule containing core material obtained in Example 28.

5

10

15

20

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		Amount compounded (W/W%)	
		Example 44	Comparative example 8
1	Polyoxyethylene(10) curing castor oil	5.00	5.00
2	Isopropyl myristate	6.00	6.00
3	Liquid paraffin #70	5.00	5.00
4	Jojoba oil	5.00	5.00
5	Magnesium stearate	0.80	0.80
6	Zinc oxide	3.00	3.00
7	Magnesium sulfate	0.30	0.30
8	conc. Glycerine	5.00	5.00
9	EDTA-2Na	0.10	0.10
10	Tocopherol acetate	1.00	1.00
11	Preservative	0.30	0.30
12	Purified water	to make 100	to make 100
A	Microcapsule	16.5	-
B	2-Ethylhexyl p-methoxycinnamate	-	10.00

[0453] SPF value of the resulting milky lotion was measured by Analysis method 8, and the results are shown below.

35

40

	SPF value
Example 44	15.7
Comparative example 8	12.4

[0454] The product was applied in an amount of 0.5 g on the back of hand, and "adhesion to skin" was evaluated by 10 panelists, the results are shown below.

45

50

Evaluation of adhesion		
Number of panelists who decided the product of Example 44 not good		3
Number of panelists who decided the product of Comparative Example 8 not good		7

[0455] The milky lotion of Example 44 was superior to that of Comparative Example 8 in adhesion onto skin.

55

Example 45, Comparative Example 9

[0456] Sunscreen creams having the following formulations were obtained in an analogous manners to that in Exam-

ple 40 and Comparative Example 4 using a microcapsule containing core material obtained in Example 13.

		Amount compounded (W/W%)	
		Example 45	Comparative example 9
1	Stearic acid	2.5	2.5
2	Cetanol	1.5	1.5
3	Vaseline	5.0	5.0
4	Liquid paraffin #70	10.0	10.0
5	Polyoxyethylene(20) oleyl ether	2.0	2.0
6	Preservative	0.3	0.3
7	Polyethyleneglycol 4000	3.0	3.0
8	Triethanol amine	2.0	2.0
9	Purified water	to make 100	to make 100
A	Microcapsule	41.70	-
B	2-Ethylhexyl p-methoxycinnamate	-	20.00

[0457] SPF value of the resulting sunscreen cream was measured by Analysis method 8, and the results are shown below.

	SPF value
Example 45	12.5
Comparative example 9	11.5

[0458] Appearance immediately after preparation and after six months are shown below

	Appearance (immediately after preparation) uniform	Appearance (after six months) uniform
Example 45	emulsification, white uniform	emulsification, white separated
Comparative example 9	emulsification, white	become yellowish

[0459] As is known from the above-described results, the microcapsule is excellent in stability with the lapse of time and prevents yellow coloration of the cream composition.

Example 46, Comparative Example 10

[0460] Hair treatments having the following formulations were obtained in analogous manners as in Example 40 and Comparative Example 4 using a microcapsule containing core material obtained in Example 22A.

		Amount compounded (W/W%)		
		Example 46	Comparative example 10	
5	1	Mixture of polyacrylamide, polyoxyethylene-sorbitoltrioleinate, liquid paraffin and volatile isoparaffin	2.0	2.0
10	2	Copolymer of poly(oxyethylene, oxypropylene) and methylpolysioxane	5.0	5.0
15	3	22-Ethylhexyl isoparmitate	2.0	2.0
20	4	Chlorinated N-[2-hydroxy-3-(palm oil alkylidimethylammonio) propyl] hydrolyzed collagen	0.3	0.3
	11	Preservative	0.3	0.3
	12	Purified water	to make 100	to make 100
	A	Microcapsule	4.9	-
	B	2-Ethylhexyl P-methoxycinnamate	-	3.0

[0461] SPF value of the resulting hair treatment was measured by Analysis method 8, and the results are shown below.

25

30

	SPF value
Example 46	6.2
Comparative example 10	5.6

[0462] The product was applied in an amount of 0.2 g on a 1g of hair bundle rinsed previously, then the hair bundle was dried. Combability was evaluated by 10 panelists, the results are shown below.

40

Evaluation of adhesion	
Number of panelists who decided the product of Example 46 good	9
Number of panelists who decided the product of Comparative Example 10 good	1

45 [0463] The hair treatments of Example 46 was superior to that of comparative Example 10 in combability.

Example 47, Comparative Example 11

[0464] Lipsticks having the following formulations were obtained in analogous manners as in Example 40 and Comparative Example 4 using a microcapsule containing core material obtained in Example 24.

55

		Amount compounded (W/W%)	
		Example 47	Comparative example 11
	1	Beeswax	7.0

(continued)

		Amount compounded (W/W%)	
		Example 47	Comparative example 11
5	2 Candelira wax	10.5	10.5
10	3 Methyl polysiloxane	11.2	11.2
15	4 Castor oil	15.0	15.0
20	5 Liquid paraffin #70	18.0	18.0
	6 Glycerin triisostearate	15.0	15.0
	7 Mica	10.0	10.0
	8 Iron oxide	3.6	3.6
	9 Red No.2	0.2	0.2
	10 Purified water	to make 100	to make 100
	A Microcapsule	5.2	-
	B 2-Ethylhexyl p-methoxycinnamate	-	3.0

[0465] SPF value of the sample prepared by diluting the resulting lipstick by 2-fold with liquid paraffin was measured by Analysis method 8, and the results are shown below.

25

	SPF value
Example 47	8.2
Comparative example 11	7.8

[0466] The results show the lipsticks of Example 47 is excellent in ultraviolet ray preventing effect.

35 Example 48, Comparative Example 12

[0467] Creams having the following formulations were obtained in analogous manners as in Example 40 and Comparative Example 4 using a microcapsule containing core material obtained in Example 28.

40

		Amount compounded (W/W%)	
		Example 48	Comparative example 12
45	1 Carboxyvinyl polymer	0.30	0.30
50	2 Potassium hydroxide	0.15	0.15
55	3 1,3-Butylene glycol	5.00	5.00
	4 Diglycerin	2.00	2.00
	5 Tetrasodium hydroxyethane-diphosphonate	0.09	0.09
	6 p-Oxybenzoate	0.25	0.25
	7 Purified water	to make 100.0	to make 100.0
	A Microcapsule	10.0	-
	B 2-Ethylhexyl p-methoxycinnamate	-	4.5

[0468] SPF value of the resulting cream was measured by Analysis method B and the results are shown below.

5

	SPF value
Example 48	5.4
Comparative example 12	5.0

10

[0469] The cream of Example 48 was excellent in ultraviolet ray preventing effect.

[0470] The skin permeability of the prepared product was measured by Analysis method 9 and the results are shown below.

15

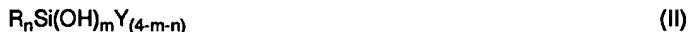
20

	Concentration in epidermis ($\mu\text{g}/\text{cm}^3$)	Concentration in hypodermis ($\mu\text{g}/\text{cm}^3$)
Example 48	1,100	2.5
Comparative example 12	4,900	50

[0471] It was recognized that the cream of Example 48 repress permeation into skin of a ultraviolet ray absorber to be compounded.

Claims

1. A microcapsule containing core material and a capsule wall, in which the capsule wall of the microcapsule comprises:
 30 organopolysiloxane synthesized by polycondensing a compound (B), monomer or monomeric mixture, wherein compound (B) contains one or more compounds represented by the general formula (II):



35

wherein m represents an integer from 1 to 4; n represents an integer from 0 to 3; $m+n \leq 4$; R represents an organic group in which a carbon atom is directly connected to a silicone atom, and when n is greater than 1, each of the R groups may be the same or different; and Y represents at least one group selected from an alkoxy group, hydrogen and siloxy group, and when $(4-m-n)$ is greater than 1, each of the groups Y may be the same or different; provided that compound (B) comprises at least one compound of formula (II) wherein $m=2$ or 3 and at least one of the R groups thereof possesses affinity for at least one of a continuous phase and a dispersed phase.

- 40 2. The microcapsule containing core material according to claim 1, wherein compound (B) is obtained by hydrolyzing a compound (A), monomer or monomeric mixture, wherein compound (A) contains one or more compounds represented by the following general formula (I):



50

wherein n represents an integer from 0 to 3; R represents an organic group in which a carbon atom is directly connected to a silicone atom, and when n is greater than 1, each of the R groups may be the same or different; and X represents at least one group selected from a hydroxyl group, hydrogen, alkoxy group, halogen group, carboxyl group, amino group and siloxy group, and when $(4-n)$ is greater than 1, each of the groups X may be the same or different; provided that compound (A) contains at least one compound of formula (I) having an R group which possesses affinity for at least one of a continuous phase and a dispersed phase.

55

3. The microcapsule containing core material according to claim 1, wherein at least one of the compounds of formula (II), which Compound (B) contains, possesses an R group carrying a hydrophilic group.

4. The microcapsule containing core material according to claim 3, wherein the hydrophilic group is a polyether or a hydrolyzed protein.
5. The microcapsule containing core material according to claim 4, wherein the hydrophilic group is a polyoxyethylene, a polyoxypropylene or a polyoxyethylene-polyoxypropylene copolymer.
- 10 6. The microcapsule containing core material according to claim 4, wherein the hydrophilic group is an N-[2-hydroxy-3-(3'-trihydroxysilyl)propoxy]propyl hydrolyzed protein or an N-[2-hydroxy-3-(3'-dihydroxymethylsilyl)propoxy]propyl hydrolyzed protein.
- 15 7. The microcapsule containing core material according to claim 5, wherein the polyoxyethylene, polyoxypropylene or polyoxyethylene-polyoxypropylene copolymer possesses a number-average polymerization degree of from 1 to 2000.
- 20 8. The microcapsule containing core material according to claim 6, wherein each of the hydrolyzed proteins possesses a number-average molecular weight of from about 100 to 50000.
9. The microcapsule containing core material according to claim 1, wherein at least one compound selected from hydrolyzable silanes and hydrolyzable polysiloxanes is present in the core material of the microcapsule.
- 25 10. The microcapsule containing core material according to claim 1 wherein a surface of the capsule wall of the microcapsule is treated at least once with a hydrolysate of at least one compound selected from hydrolyzable silanes and hydrolyzable polysiloxanes.
11. The microcapsule containing core material according to claim 1, wherein a surface of the capsule wall is treated with a compound (A), monomer or monomeric mixture, wherein compound (A) contains one or more compounds represented by the general formula (I) as defined in claim 2.
- 30 12. The microcapsule containing core material according to claim 9 or 10, wherein at least one compound selected from hydrolyzable silanes and hydrolyzable polysiloxanes is methyltrichlorosilane, methyldichlorosilane, dimethyl-dichlorosilane, trimethylchlorosilane, phenyltrichlorosilane, diphenyldichlorosilane, methyltrimethoxysilane, methyl-triethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, hexyltrimethoxysilane, octyltriethoxysilane, decyltrimethoxysilane, tetramethoxysilane, tetraethoxysilane or $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_f(\text{Me}_2\text{SiO})_g\text{SiMe}_3$, wherein f represents an integer from 5 to 50, and g represents an integer from 2 to 100 and Z represents hydrogen or an alkoxy group.
- 35 13. A method for producing a microcapsule containing core material and a capsule wall, which comprises the following sequential steps;
- 40 (1) producing a compound (B), monomer or monomeric mixture, by hydrolysis of a compound (A), monomer or monomeric mixture, wherein compound (B) contains one or more compounds represented by the general formula (II) as defined in claim 1 wherein compound (A) contains one or more compounds represented by general formula (I) as defined in claim 2
- 45 (2) polycondensating, by neutralizing, compound (B) to form a prepolymer;
- (3) mixing and emulsifying the prepolymer with a core material and/or a second liquid phase; and
- (4) curing the capsule wall of said microcapsule by further polycondensating the prepolymer.
- 50 14. The method for producing the microcapsule containing core material according to Claim 13, wherein the steps of producing compound (B) by hydrolysis of compound (A) and polycondensating of compound (B) to form a prepolymer are each conducted in a medium having a viscosity of 10 to 2000 mPa · s before addition of compound (A).
15. The method for producing the microcapsule containing core material according to Claim 14, wherein the media is an aqueous gelatin solution having a viscosity of 10 to 2000 mPa · s.
- 55 16. The microcapsule containing core material according to claim 1, wherein the core material contains an ultraviolet absorber.
17. The microcapsule containing core material according to claim 16, wherein the ultraviolet absorber is 2-ethylhexyl

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p-methoxycinnamate or 4-tert-butyl-4'-methoxydibenzoylmethane.

18. An agent or preparation which comprises a microcapsule containing core material according to claim 16.
- 5 19. The agent or preparation according to claim 18 which is a cosmetic or a pharmaceutical preparation.
20. The agent or preparation according to claim 19 wherein said agent or preparation is applied to the skin or hair.

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